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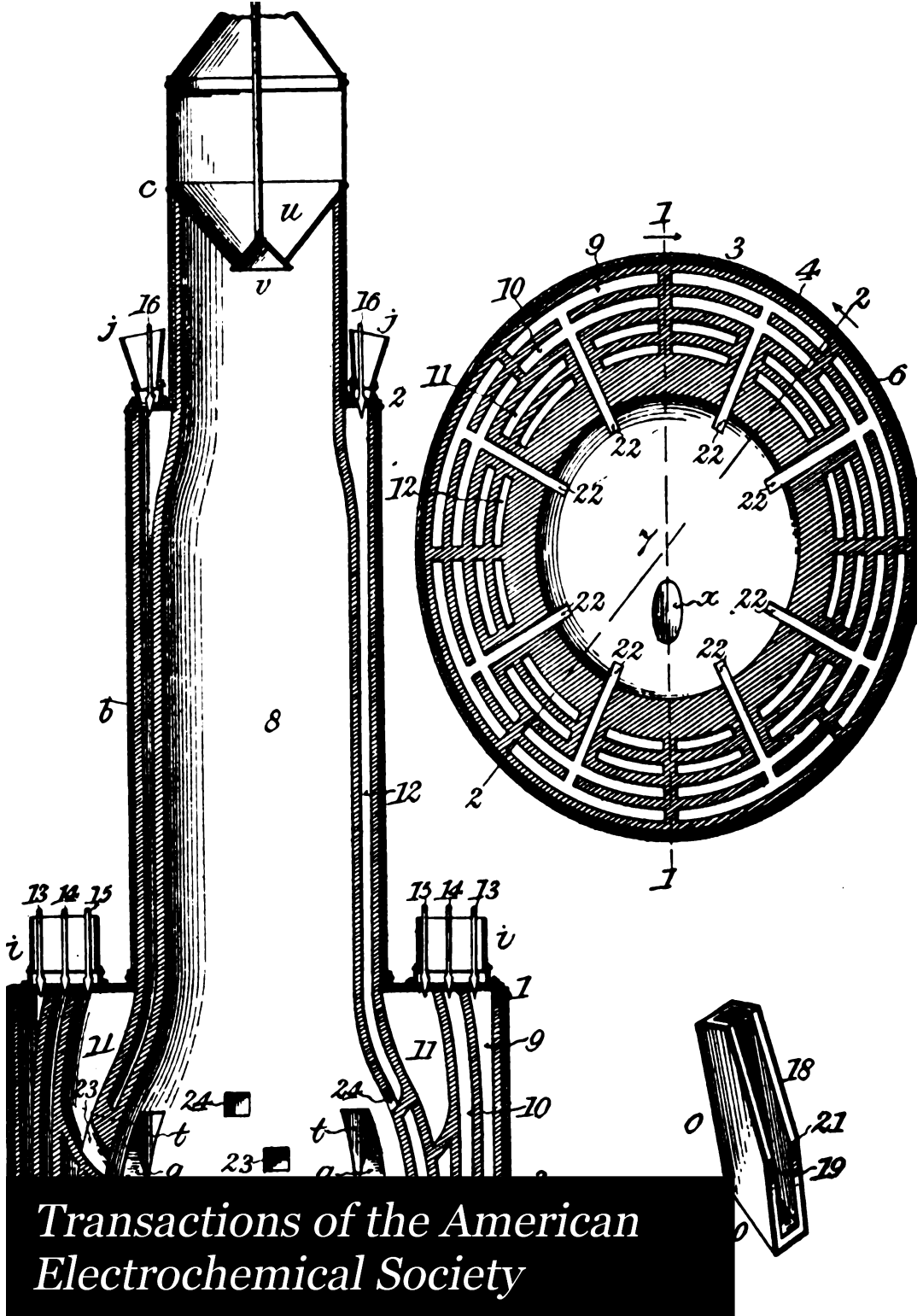

Transactions of the American Electrochemical Society

American Electrochemical Society

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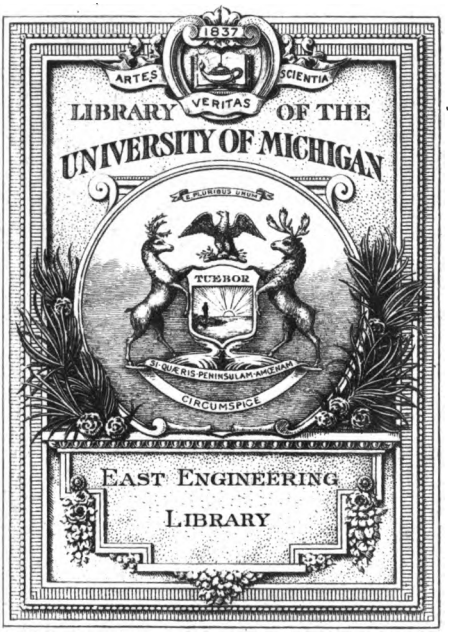

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TRANSACTIONS

OF THE

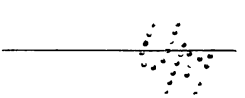
AMERICAN

ELECTROCHEMICAL SOCIETY

VOLUME II.

SECOND MEETING.

NIAGARA FALLS, SEPTEMBER 15, 16, 17, 18, 1902.



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1902.

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TABLE OF CONTENTS.

05-24-28 R.J.

PAGE

Proceedings of Second Meeting 1
Abstract of Proceedings of Board of Directors 6
Catalogue of Members, Alphabetical 9
Catalogue of Members, Geographical 30

PAPERS.

On the Testing of Carbon Electrodes.—FitzGerald 43
The Efficiency of Electric Furnaces.—Richards 51
Cathodic Reduction.—Weightman 65
Differences of Potential between Metallic Cadmium and Solutions of Cadmium Iodide in Various Solvents.—Kahlenberg 89
Developments in the Electrometallurgy of Iron and Steel.—Ruthenburg 93
On the Fusion of Quartz in the Electric Furnace.—Hutton 105
Voltaic Cells with Fused Electrolytes.—Byrnes 113
A Thermo-electric Theory of Concentration Cells.—Carhart 123
An Electrochemical Paradox.—Hering 139
Electrochemistry at the World's Fair, St. Louis.—Goldsborough 153
The Electronic Hypothesis and Its Applications.—Reuterdahl 159
The Electrolytic Dissolution of Soluble Metallic Anodes.—Johnson 171
Storage Battery Invention.—Rodman 177
Some Advances in the Closed and Continuous-Working Electric Furnace.—Taylor 185
The Phenomenon of the Formation of Metallic Dust from Cathodes.—Haber 189
The Theory and Practice of Continuous-Flow Electric Calorimetry.—Barnes 197
A Unit of Electrical Quantity for Use in Electrochemical Calculations.—Cowles 207
Pumps and Other Accessories in Electrolytic Plants.—Browne and Vorce 219
Some Phenomena of Electrolytic Conduction.—Reed 235
Electrochemical Polarization.—Langley 255
A Contribution to the Electrochemistry of Barium Compounds.—Haff .. 267
Index of Subjects and Authors 271
Advertisements.

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Term expires 1903.

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CHAS. A. DOREMUS, Ph.D.,
W. R. WHITNEY, Ph.D.
Terms expire 1903.

CHARLES M. HALL,
LOUIS KAHLENBERG, Ph.D.,
HENRY S. CARHART, Ph.D.
Terms expire 1904.

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Terms expire 1903.

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Terms expire 1904.

CARL HERING,
W. D. WEAVER,
E. F. ROEBER, Ph.D.
Terms expire 1905.

TREASURER:

PEDRO G. SALOM, 408 Bourse Building, Philadelphia, Pa.
Term expires 1903.

SECRETARY:

CHAS. J. REED, 929 Chestnut St., Philadelphia, Pa.
Term expires 1903.

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C. J. REED, ... Secretary.
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VOLUME II. 1902.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS.

CONDENSED MINUTES OF THE SECOND MEETING OF THE SOCIETY, HELD AT NIAGARA FALLS, SEPTEMBER 15-18, 1902 :
(Number of members registered, 117 ; number of guests, 47 ; total, 164.)

SESSION OF SEPTEMBER 15TH.

The meeting was called to order by President Richards, at 10 A.M., in the parlor of the International Hotel. The chairman congratulated the Society on the large attendance, and read the following letter of greeting from the Deutsche Electrochemische Gesellschaft, sent in response to a communication sent to that society at their Spring meeting.

Professor Joseph W. Richards, President of the American Electrochemical Society :

DEAR SIR :—

Your kind letter of greeting of the 28th. April reached us in Würzburg just after the close of our General Meeting, but in time to lay the same before our members during the festival dinner.

From all present the formation of The American Electrochemical Society was greeted with particular pleasure, and we were instructed to convey the heartiest congratulations of our Society to you, to express our most earnest hopes for its prosperity and

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development, and at the same time to assure you that we shall always follow your work with the greatest interest and that we sincerely trust that a continuous close and amicable connection will remain between ourselves and your highly esteemed Society.

May the result of our united work tend to promulgate the further advance of our particular science and the technical utilization of our researches for the benefit of the world at large.

We trust that you and your friends will maintain and preserve your kind sentiments for us under our new name, especially as we assure you that our interest in electrochemistry will be maintained in the future as earnestly as in the past.

Will you kindly present our united best wishes and regards to your friends, and assure them of the particular pleasure it will afford us to be able to greet them at our next annual meeting, which will be combined with the Fifth International Congress for Applied Chemistry, to be held next year at Whitsuntide, in Berlin; please accept for yourself the assurance that we remain,

Yours most sincerely,

DEUTSCHE ELECTROCHEMISCHE GESELLSCHAFT.

The President, *The Vice-President*,

May 24, 1902. J. H. VAN'T HOFF. DR. BÖTTINGER.

The chair then introduced to the meeting Doctor Fritz Haber, of the Technical School of Karlsruhe, Germany, who was present as the guest of the Society and the official representative of the Deutsche Bunsen Gesellschaft (formerly Deutsche Electrochemische Gesellschaft). Dr. Haber presented the following communication from his society.

To the President of the American Electrochemical Society.

DEAR SIR:—We beg to tender you our sincerest thanks for your kind invitation to attend your second meeting, and greatly regret that we personally are unable to be with you and take part in your interesting discussions. We allow ourselves, however, to introduce, by this letter, Professor Haber, from Karlsruhe, delegated by the former "Electrochemische Gesellschaft," now "Bunsen Gesellschaft," who will be with you in order to verbally assure you and your esteemed Society of the great interest we take in your development and in your work, which will doubtless propagate still further the new science in which we are all so deeply interested.

Will you, dear Mr. President, kindly express to your friends, in the name of our Society, our heartiest and sincerest wishes for your continuous welfare, and especially for the maintenance of

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the agreeable and cordial friendship which already exists between your esteemed Society and ourselves.

We remain, yours sincerely,

for the DEUTSCHE BUNSEN GESELLSCHAFT,

The President,

September 9, 1902. DR. BÖTTINGER.

Dr. Haber's formal remarks were made later, as a preface to the reading of his paper, and will be found as an introduction to his paper, printed in the Transactions.

The chair then called upon the treasurer, Mr. P. G. Salom, for some remarks on the condition of the Society's finances.

The treasurer reported that the total receipts to date, from membership dues and sale of Transactions, were $1979.47 ; total expenses, $712.99 ; balance, $1266.48 ; amount still due from various sources, $325 ; total assets, $1591.48 ; unpaid bills, $641.64, leaving a net balance of $949.84. This balance was estimated as sufficient for the publication of Volume II of our Transactions, due to our members and chargeable against this year's dues.

Papers by Mr. F. A. J. Fitzgerald, of Niagara Falls, N. Y., Dr. J. W. Richards, of Bethlehem, Pa., Mr. A. T. Weightman, of Niagara Falls, N. Y., and Dr. L. Kahlenberg, of Madison, Wis., were then read and discussed, as published in full in the Transactions. The afternoon was spent in visits to industrial establishments.

After Professor Kahlenberg's paper, the following remarks and motion were made by Vice-President Chas. A Doremus.

MR. PRESIDENT : Before we adjourn I would like to bring a matter before the meeting which may be of special interest to us not only as a body, but also as individuals. The Fifth International Congress of Applied Chemistry is to be held next June in Berlin, under the auspices of the German government, with meetings at the Reichstag Gebäude. One of the important sections is the Electrochemical Section, and this Society should be represented in Berlin by prominent delegates. I trust the Board of Directors of the Society or the meeting at large will see to it that we have such men appointed as will be interested in the work of the Congress.

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I therefore move, Mr. President, that the Board of Managers be requested to take action regarding the appointment of delegates to the Fifth International Congress of Applied Chemistry to be held in Berlin in 1903.

MR. HABER: Mr. President, I believe I am entitled to say that we will be very glad, in Germany, to meet every one who comes to visit us from your Society. It is to be hoped that many of you will give us the honor of meeting you in Berlin next year.

The motion was seconded and carried.

SESSION OF SEPTEMBER 16th.

The meeting was held at 10 A.M., in the auditorium of the Natural Food Company's Building.

Papers by Mr. M. Ruthenberg, of Philadelphia, Professor R. S. Hutton, of Manchester, England, Dr. E. A. Byrnes, of Washington, D. C., Mr. Carl Hering, of Philadelphia, and Professor H. S. Carhart, of Ann Arbor, Mich., were read and discussed, as printed in full in the Transactions. The afternoon was spent in visits to establishments in the vicinity.

SESSIONS OF SEPTEMBER 17, 1902.

The morning session was held at 9.30 A.M., in the parlor of the International Hotel.

Papers by Professor W. E. Goldsborough, of Lafayette, Ind., Professor H. T. Barnes, of Montreal, Mr. A. Reuterdahl, of Providence, R. I., Mr. W. McA. Johnson, of New Brighton, Staten Island, N. Y., and Mr. H. Rodman, of Philadelphia, were read and discussed, as printed in full in the Transactions.

Following the discussion of Professor Goldsborough's paper, on motion of Mr. Carl Hering, the following resolution was adopted:

WHEREAS: The American Electrochemical Society, in convention assembled, recognizes the great international importance of the Louisiana Purchase Exposition, and feels that it will do much in placing before the peoples of the world a true picture of our national progress, and

WHEREAS: In no branch of our scientific or industrial progress have greater developments taken place recently than in the field of electrochemistry,

Resolved, That the American Electrochemical Society hears with great satisfaction the announcement that steps are being taken looking to the organization of a fine and comprehensive ex-

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hibit in the group of electrochemistry, and offers assurances of hearty good-will and cooperation in the accomplishment of this much-to-be-desired end.

Dr. E. A. Byrnes asked for the privilege of the floor, which being granted, he stated that a company engaged in developing one of the largest water-powers in this country authorized the statement that it would furnish free electrical energy in indefinite amount, for a considerable period, to any industry locating with that company.

The afternoon session was held at 3 P.M., at the same place.

Papers by Dr. F. Haber, of Karlsruhe, Germany, Mr. A. H. Cowles, of Cleveland, Ohio, and Mr. E. P. Taylor, of Penn Yan, N. Y., were read and discussed, as printed in full in the Transactions.

On the evening of September 17th, about 150 members and guests sat down to banquet at the International Hotel, followed by a ball, the whole being at the invitation of the Niagara Falls members of the Society.

SESSION OF SEPTEMBER 18TH.

The meeting was held at 9.30 A.M., in the parlor of the International Hotel.

Papers by Mr. D. H. Browne, of Cleveland, Ohio, Mr. M. M. Haff, of Niagara Falls (by title only), Dr. J. W. Langley, of Cleveland, Ohio, and Mr. C. J. Reed, of Philadelphia, were read and discussed, as printed in full in the Transactions.

On motion of Mr. Hering, seconded by Dr. Kahlenberg, the thanks of the Society were extended to the following, for what they did to contribute towards the success of the meeting, and for inviting the Society to visit their works:

The Local Committee of the Society (the resident members), The Ladies' Committee, The Natural Food Company, The Niagara Power Company, The Hydraulic Power and Manufacturing Company, The Electrical Lead Reduction Company, The International Acheson Graphite Company, The Carborundum Company, and The Atmospheric Products Company.

C. J. REED,
Secretary.

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BOARD OF DIRECTORS.

ABSTRACTS FROM THE MINUTES OF THE MEETINGS OF THE BOARD OF DIRECTORS AND OF ITS EXECUTIVE COMMITTEE, APRIL-SEPTEMBER, 1902.

The Board held five stated monthly meetings, and the Executive Committee several additional ones, in the above interval, at which the following action was taken on matters of interest to the Society at large :

Reprints of papers, with discussion thereon, published by the Society, will be furnished free to the authors, to the number of 50 copies, without covers. Covers, and all additional copies above 50, will be furnished to the authors at cost.

Regular meetings of the Executive Committee of the Board of Directors are held on the first Thursday of each month, at the office of the Society, 929 Chestnut St., Philadelphia, at 12.30 P.M.

At the meeting of the Board at Niagara Falls, September 15th, at which 16 out of the 18 members of the Board were present, the secretary reported that the number of members added since April was 35, making altogether 390; applicants, 24; total, 414. Mr. Carl Hering made a statement as to the large amount of work which had been performed gratuitously by the secretary, and it was moved that he be compensated, but the secretary stated that he would decline to accept payment for such services, even if action were taken.

On motion, the Executive Committee was authorized to supply the Transactions, bound in cloth, to members without extra cost, beginning with Vol. II.

The following were elected to membership at the stated monthly meetings :

July 3, 1902.

Edgar F. Price, Niagara Falls ; George H. Brill, Chicago ; Edward L. Anderson, St. Louis ; Loren Gleason Waite, New York ; Arthur Clarke Melcher, Newton Centre, Mass.; David Pepper, Jr., Philadelphia ; Wm. F. Doerflinger, Niagara Falls ;

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Chas. M. Thomas, Nutley, N. J.; Henry E. Gruner, Basel, Switzerland; Dr. G. G. Pond, State College, Pa.

August 7, 1902.

Dr. Edward Hart, Easton, Pa.; Arthur Lathwood, Niagara Falls; Isaac Russell Edmunds, Sault Ste. Marie, Mich.; Professor Henry M. Howe, New York; Thomas E. Steere, Niagara Falls; James MacMahon, Niagara Falls; Charles P. Steinmetz, Schenectady, N. Y.; Dr. Wm. H. Walker, Boston; D. L. Davis, Salem, Ohio; George L. Bixby, Cleveland, Ohio.

September 4, 1902.

Professor Dr. Nicolas Piltschikoff, Kharkov, Russia; Professor Dr. Richard Lorenz, Zurich, Switzerland; Dr. Henry T. Böttinger, president of the Deutsche Bunsen Gesellschaft, Elberfeld, Germany; J. A. Capp, Schenectady, N. Y.; Stanislaus P. Franchot, Niagara Falls; Walter B. Bishop, Grand Forks, B. C.; Charles B. Barton, Berlin, N. H.; Wyatt Hamilton Allen, San Francisco; Robert Anton Fliess, East Orange, N. J.; Sol. D. Benoliel, Niagara Falls; Aldus C. Higgins, Worcester, Mass.; F. M. Perkin, Forest Hill, London, England; George N. Jepson, Worcester, Mass.; Robert T. Frazier, Washington, D. C.; Oliver P. Fritchle, Denver.

October 2, 1902.

Halbert K. Hitchcock, Floreffe, Pa.; Robert A. Witherspoon, Niagara Falls, N. Y.; Edwin J. Murphy, Lynn, Mass.; G. A. Burr, Etzatlau, State of Jalisco, Mexico; Mrs. M. J. Reed, Philadelphia, Pa.; John P. Jackson, State College, Pa.; Willard E. Case, Auburn, N. Y.; Arthur E. Gibbs, Niagara Falls, N. Y.; J. C. Roberts, Niagara Falls, N. Y.; C. G. Herbert, Detroit, Mich.; W. O. Snelling, Union City, Pa.; Max M. Haff, Niagara Falls, N. Y.; Samuel Weil, Niagara Falls, N. Y.; Edwin J. Houston, Philadelphia, Pa.; Lewis E. Saunders, Niagara Falls, N. Y.; George W. Fletcher, Brooklyn, N. Y.; Ernst J. Berg, Schenectady, N. Y.; Isaiah L. Roberts, Wall St., New York; Wesley S. Block, New York; Henry Arden, San Francisco, Cal.; Oscar Pickering, Cleveland, Ohio; Ray Hill White, Niagara Falls, N. Y.; Loren R. Vorce, Cleveland, Ohio.

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November 6, 1902.

Erik W. Tillberg, Worcester, Mass.; George W. Patterson, Jr., Ann Arbor, Mich.; A. A. Knudson, New York; Arthur E. Kennelly, Cambridge, Mass.; Chas. S. Bradley, New York; Walter T. Taggart, Philadelphia; Barthold E. Schlessinger, Boston; Max Mauran, Niagara Falls; W. E. Goldsborough, Lafayette, Ind.; C. C. Speiden, Summit, N. J.; F. B. Crocker, New York; Charles J. Greenstreet, Ford City, Pa.; Ashmead G. Rodgers, Niagara Falls; F. J. A. McKittrick, Schenectady, N. Y.; Wm. O. Mathews, Dover Bay, Ohio; E. A. Deeds, Niagara Falls; Dr. A. T. Lincoln, Urbana, Ill.; J. G. Zimmerman, Madison, Wis.; James L. Ewin, Washington, D. C.; Geo. O. Knapp, Chicago; C. E. Freeman, Chicago; Charles F. Vaughn, Niagara Falls; Harold Childs Pease, Schenectady, N. Y.; Professor Dr. Fritz Haber, Karlsruhe, Germany.

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AMERICAN ELECTROCHEMICAL SOCIETY.

CATALOGUE OF MEMBERS.

(November 6, 1902.)

		Date of election. [Members of date April 3, 1902, are charter members.]
Acheson, E. G.	International Acheson Graphite Company, Niagara Falls, N. Y.	Apr. 3, 1902
Acker, Charles E.	Acker Process Company, Niagara Falls, N. Y.	Apr. 3, 1902
Adams, Prof. Comfort A.	Assistant Professor of Electrical Engineering, Harvard University, Res. 13 Farrar St., Cambridge, Mass.	Apr. 3, 1902
Adams, Ernest K.	455 Madison Ave., New York.	Apr. 3, 1902
Adams, Geoffrey C., C.E., M.A.	Chief Engineer, Columbian Carbide Company, 29 Broadway, New York.	Apr. 3, 1902
Adams, Dr. Isaac	1776 Massachusetts Ave., Cambridge, Mass.	Apr. 3, 1902
Addicks, Lawrence	Raritan Copper Works, Perth Amboy, N. J.	Apr. 3, 1902
Alden, John	Pacific Mills, Lawrence, Res. Andover, Mass.	Apr. 3, 1902
Allen, Wyatt H.	Consulting Engineer, 331 Pine St., San Francisco, Cal.	Sep. 4, 1902
Amster, N. L.	Consulting Mining Engineer, 32 Equitable Building, Boston, Mass.	Apr. 3, 1902
Anderson, Edw. L.	Electrochemist, Anderson Electric Mfg. Company, 119 N. 11th St., St. Louis, Mo., Res. 2700 Euclid Ave., St. Louis, Mo.	July 3, 1902
Arden, Henry B. A.	Electro-Metallurgist, for Dr. H. L. Wagner, 900 Pine St., San Francisco, Cal.	Oct. 2, 1902
Askew, C. B.	Consulting Engineer, 1652 Monadnock Building, Chicago, Ill.	Apr. 3, 1902
Atwood, Geo. F.	Western Electric Company, New York.	Apr. 3, 1902
Austen, Peter T., Ph.D., F.C.S.	80 Broad St., New York.	Apr. 3, 1902
Bakewell, Thos. W.	Patent Lawyer, Carnegie Building, Pittsburgh, Pa.	Apr. 3, 1902

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		Date of election.*
Bancroft, Wilder D., Ph.D.	Cornell University, Ithaca, N. Y.	Apr. 3, 1902
Banks, Wm. C.	Gordon Battery Company, 439-445 E. 144th St., New York.	Apr. 3, 1902
Barker, E. R.	Burgess Sulphite Fibre Co., Berlin, N. H.	Apr. 3, 1902
Barnes, H. T., Ph.D.	McGill University, Montreal, Can.	Apr. 3, 1902
Barnes, S. G.	Electrical Engineer, Solvay Process Co., 310 Boulevard West, Detroit, Mich.	Apr. 3, 1902
Barr, B. M.	234 E. 21st St., Flatbush, L. I.	Apr. 3, 1902
Barstow, W. S.	Consulting Engineer, Bowling Green Offices, New York, Res. 868 Park Place, Brooklyn, N. Y.	Apr. 3, 1902
Bartol, H. W.	31, Bd. Victor Hugo, Nice, France.	Apr. 3, 1902
Barton, Chas. B.	Superintendent of Electrolytic Bleach Plant, Burgess Sulphite Fibre Co., Berlin, N. H.	Sep. 4, 1902
Batchelor, Chas.	52 Broadway, New York.	Apr. 3, 1902
Bates, Wm. S.	Consulting Engineer, 510 Boylston Building, Chicago, Ill.	Apr. 3, 1902
Becket, Fred. M.	170 Buffalo Ave., Niagara Falls, N. Y., Box 158.	Apr. 3, 1902
Behrend, Dr. Otto F.	Erie, Pa.	Apr. 3, 1902
Benoliel, Sol. D., B.S., E.E., A.M.	Roberts Chemical Company, Res. 14 C St., Niagara Falls, N. Y.	Sep. 4, 1902
Berg, Ernst J.	Electrical Engineer, General Electric Company, Schenectady, N. Y.	Oct. 2, 1902
Betts, Anson G.	Troy, N. Y.	Apr. 3, 1902
Bierbaum, C. H.	Lumen Bearing Co., 1155 Sycamore St., Res. 312 Prospect Ave., Buffalo, N. Y.	Apr. 3, 1902
Bishop, Walter B.	Assistant Assayer, Granby Smelting, Mining & Power Co., Grand Forks, B. C.	Sep. 4, 1902
Bixby, George L.	Assisiant Treasurer and Superintendent The Willard Storage Battery Co., 49 Wood St., Cleveland, Ohio.	Aug. 7, 1902
Blackmore, Henry S.	Mount Vernon, N. Y.	Apr. 3, 1902
Bleecker, John S.	Stone and Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902

* Members of date April 3, 1902, are charter members.

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		Date of election.*
Block, Wesley S.	President Roberts Chemical Company, 40 Wall St., New York.	Oct. 2, 1902
Böttinger, Dr. H. T.	President of *Deutsche Bunsen Gesellschaft*, Berlin, Res. Elberfeld, Germany.	Sep. 4, 1902
Bogue, Chas. J.	Manufacturer of Electric Machinery, 213-215 Center St., New York	Apr. 3, 1902
Bolling, Randolph	Superintendent of the Victoria Furnace, Goshen, Va.	Apr. 3, 1902
Boon, Prof. John D.	School of Physics and Chemistry, John Tarleton College, Stephenville, Tex.	Apr. 3, 1902
Bostick, E. E.,M.D.	American Synthetic Company, 3600 N. 5th St., Philadelphia, Pa.	Apr. 3, 1902
Bowman, Walker	39 Cortlandt St., New York.	Apr. 3, 1902
Boynton, Dr. C. S.	Burlington, Vt.	Apr. 3, 1902
Bradley, Chas. S.	President Atmospheric Products Co., 44 Broad St., New York.	Nov. 6, 1902
Bradley, Prof. Walter M.	Sheffield Scientific School, Chemical Laboratory, Res. 1346 Chapel St., New Haven, Conn.	Apr. 3, 1902
Brill, Geo. M.	Consulting Engineer, 1134 Marquette Building, Res. 6510 Yale Ave., Chicago, Ill.	July 3, 1902
Brindley, Geo. F.	Niagara Electro-Chemical Co., Niagara Falls, N. Y.	Apr. 3, 1902
Brock, Robert C. H.	1612 Walnut St., Philadelphia, Pa.	Apr. 3, 1902
Brooks, Prof. Morgan	University of Illinois, Urbana, Ill.	Apr. 3, 1902
Brown, Harold P.	Electrical Engineer, 120 Liberty St., New York.	Apr. 3, 1902
Brown, J. Stanford	489 Fifth Ave., New York.	Apr. 3, 1902
Brown, Oliver W.	Instructor on Electrochemistry, Indiana University, Bloomington, Ind.	Apr. 3, 1902
Brown, W. G.,B.S., Ph.D.	Professor of Chemistry, University of Missouri, Columbia, Mo.	Apr. 3, 1902
Browne, David H.	Chief Chemist, Canadian Copper Co., 12 Wade Building, Res. 115 Archwood Ave.,Cleveland, Ohio.	Apr. 3, 1902
Browne, William Hand, Jr.	Editor Electrical Review, Park Row Building, New York, Res. 431 Beech St., Richmond Hill, New York.	Apr. 3, 1902

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		Date of election.*
Buchanan, Leonard B.	Stone & Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Burbank, Prof. J. E.	Instructor on Physics, University of Maine, Orono, Me.	Apr. 3, 1902
Burgess, Prof. C. F.	University of Wisconsin, Madison, Wis.	Apr. 3, 1902
Burr, G. A.	Engineer and Superintendent of Mines, The Hidalgo Mining Company, Etzatlan, State of Jalisco, Mex.	Oct. 2, 1902
Byrnes, Eugene A., Ph.D.	Patent Lawyer, 918 F Street, N. W., Res. 2539 13th St., Washington, D. C.	Apr. 3, 1902
Caldwell, Edward	114 Liberty St., New York, Res. 50 Westervelt Ave., Plainfield, N. J.	Apr. 3, 1902
Cameron, Walter S.	239 W. 136th St., New York	Apr. 3, 1902
Capp, J.A.	Chief of Testing Laboratory, General Electric Company, Schenectady, N.Y.	Sep. 4, 1902
Carhart, H. S., LL.D.	University of Michigan, Ann Arbor, Mich.	Apr. 3, 1902
Carnaghan, E. D.	Villa Corono, Durango, Do., Ventanas, Consolidated Mining & Milling Co., Mexico.	Apr. 3, 1902
Carveth, Prof. Hector R.	Cornell University, Ithaca, N. Y.	Apr. 3, 1902
Case, Willard E.	Auburn, N. Y.	Oct. 2, 1902
Cheney, W. C.	Electrical Engineer, Park Place, Portland, Ore., Box 449.	Apr. 3, 1902
Chiaraviglio, Ing. Dino.	32 Piazza Di Spagna, Rome, Italy.	Apr. 3, 1902
Childs, D. H.	New Kensington, Pa.	Apr. 3, 1902
Clamer, G. H.	Ajax Metal Co., Philadelphia, Pa.	Apr. 3, 1902
Clare, James P.	51 Edison St., Quincy, Mass.	Apr. 3, 1902
Clark, Friend E.	New Martinsville, W. Va.	Apr. 3, 1902
Clark, Wm. J.	The British Thomson-Houston Co., Ltd., Rugby, Eng.	Apr. 3, 1902
Coggeshall, G. W.	620 Atlantic Ave., Res. Chestnut St., Dedham, Mass.	Apr. 3, 1902
Coho, H. B.	Contracting Engineer, 149 Broadway, New York.	Apr. 3, 1902
Coit, Chas. Welles	United Barium Co., Niagara Falls, N.Y.	Apr. 3, 1902
Coit, Dr. Jas. Milnor	St. Paul's School, Concord, N. H.	Apr. 3, 1902

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		Date of election.*
Colby, Edward A.	Baker Platinum Works, Newark, N. J.	Apr. 3, 1902
Collins, C.L., 2nd	International Acheson Graphite Co., 315 Buffalo Ave., Niagara Falls, N. Y.	Apr. 3, 1902
Cowles, Alfred H.	361 The Arcade, Res. 656 Prospect St., Cleveland, Ohio.	Apr. 3, 1902
Cox, G. E.	Superintendent Union Carbide Works, 315 Buffalo Ave., Niagara Falls, N. Y.	Apr. 3, 1902
Creighton, Elmer E.F.	Stanley Electric Mfg. Co., Pittsfield, Mass.	Apr. 3, 1902
Crocker, F.B., Ph.D.	Professor of Electrical Engineering, Columbia University, Res. 14 W. 45th St., New York.	Nov. 6, 1902
Darling, Jas. D.	Harrison Bros. & Co., 35th St. and Gray's Ferry Road, Philadelphia, Pa.	Apr. 3, 1902
Davis, D. L.	Superintendent The Salem Electric Light and Power Co., Salem, Ohio.	Aug. 7, 1902
Davis, H. J.	65 Wall St., New York.	Apr. 3, 1902
Deeds, Edward A.	Factory Manager, The National Food Company, Niagara Falls, N. Y.	Nov. 6, 1902
Dodge, Norman	Electric Storage Battery Co., 19th St. and Allegheny Ave., Philadelphia, Pa.	Apr. 3, 1902
Doerflinger, William, F., B.S.	Chief Chemist, Acker Process Co., Niagara Falls, N. Y.	July 3, 1902
Doggett, Chas. S.	Niagara Falls, N. Y., Res. East Chicago, Ind.	Apr. 3, 1902
Donaldson, Wm. W.	Gould Storage Battery Co., 25 W. 33rd St., New York.	Apr. 3, 1902
Doney, D. C.	De Lamar Copper Refining Works, Carteret, N. J., 518 Monroe Ave., Elizabeth, N. J.	Apr. 3, 1902
Doremus, Chas. A., M.D., Ph.D.	17 Lexington Ave., New York.	Apr. 3, 1902
Dow, Herbert H.	Midland, Mich.	Apr. 3, 1902
Drown, T. M.	President Lehigh University, South Bethlehem, Pa.	Apr. 3, 1902
Dunn, Clifford E.	Counsellor-at-Law, 13-21 Park Row, New York.	Apr. 3, 1902
Durant, Edw., E.E.	Electrical Engineer, Ward's Island, Res. 115 E. 26th St., New York.	Apr. 3, 1902
Easterbrooks, F. D.	Raritan Copper Works, Perth Amboy, N. J.	Apr. 3, 1902

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		Date of election.*
Eddy, A. H.	Electrician and Chemist, Eddy Electric Mfg. Co., Windsor, Conn.	Apr. 3, 1902
Edmands, I. R.	Electrical Engineer and Superintendent Union Carbide Co., Sault Ste. Marie, Mich.	Aug. 7, 1902
Elliott, Arthur H.	Consolidated Gas Company, 4 Irving Place, New York.	Apr. 3, 1902
Elworthy, H. S.	Consulting Chemical Engineer, 239 Dashwood House, 9 New Broad St., London, E. C., England.	Apr. 3, 1902
Ely, Theodore N.	P. R. R. Co., Chief of Motive-Power, Broad-Street Station, Philadelphia, Pa.	Apr. 3, 1902
Emery, Arthur L.	Chemical and Mining Engineer, Indiana and 24th Sts., San Francisco, Cal.	Apr. 3, 1902
Evans, Herbert S.	Instructor on Electrical Engineering, University of Nebraska, Lincoln, Neb.	Apr. 3, 1902
Evans, J. W.	Civil and Mining Engineer, Deseronto, Ontario, Can.	Apr. 3, 1902
Ewin, James L.	Patent Solicitor, 900 F St., N. W., Washington, D. C.	Nov. 6, 1902
Eyles, A. H.	Addingham, Pa.	Apr. 3, 1902
Falding, Fred. J.	Consulting Engineer, 52 Broadway, New York.	Apr. 3, 1902
Fielding, F. E.	Virginia City, Nevada.	Apr. 3, 1902
FitzGerald, F. A. J.	Chemist, International Acheson Graphite Co., Niagara Falls, N. Y., P. O. Box 118.	Apr. 3, 1902
FitzGibbon, R.	77 John St., New York.	Apr. 3, 1902
Fitzmaurice, Jas. S.	General Post Office, Sydney, Australia.	Apr. 3, 1902
Flanders, Louis H.	Westinghouse Machine Co., Pittsburgh, Pa.	Apr. 3, 1902
Fleming, R.	General Electric Co., Lynn, Mass.	Apr. 3, 1902
Fletcher, Geo. W., E.E.	Engineer, Hadaway Electric Heating and Engineering Co.; Res. 38 Grove St., Brooklyn, N. Y.	Oct. 2, 1902
Fliess, Robert A.	Superintendent Testing Dept. Edison Storage Battery Co., Montclair, N. J., Res. 44 Chestnut St., East Orange, N. J.	Sep. 4, 1902
Foersterling, Dr. Hans	Roessler & Hasslacher Chemical Co., Perth Amboy, N. J.	Apr. 3, 1902

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		Date of election.*
Forbes, Francis	Counsellor-at-Law, 34 Nassau St., Res. 8 W. 56th St., New York.	Apr. 3, 1902
Fowler, Samuel S.	Mining Engineer, Nelson, B. C.	Apr. 3, 1902
Fraley, Jos. C.	Attorney-at-Law, 929 Chestnut St., Res. 1833 Pine St., Philadelphia, Pa.	Apr. 3, 1902
Franchot, Stanislas P.	General Manager National Electrolytic Co., Niagara Falls, N. Y.	Sep. 4, 1902
Frankforter, Prof. G. B.	University of Minnesota, Minneapolis, Minn.	Apr. 3, 1902
Frazier, Robert T.	918 F St., N. W., Res. 3016 13th St., Washington, D. C.	Sep. 4, 1902
Freedman, W. H.	Professor of Electrical Engineering, University of Vermont, Burlington, Vt.	Apr. 3, 1902
Freeman, C. E.	Associate Professor Electrical Department, Armour Institute, Chicago, Ill.	Nov. 6, 1902
Fritchle, Oliver P.	Chief Chemist, Boston & Colorado Smelting Company, Argo, Colo., Res. 1618 Pennsylvania Ave., Denver, Colo.	Sep. 4, 1902
Gabriel, George A.	Box 390, Cumberland Mills, Me.	Apr. 3, 1902
Garduno, Jesus	Aguascalientes, Mexico.	Apr. 3, 1902
Gerry, M. H., Jr.	General Manager and Chief Engineer Missouri River Power Co., Helena, Montana.	Apr. 3, 1902
Gibbs, Arthur E.	Chemist, The National Electrolytic Co., Niagara Falls, N. Y.	Oct. 2, 1902
Gibbs, W. T	Vermilion Chemical Co., Niagara Falls, N. Y.	Apr. 3, 1902
Gifford, Wm. E.	59 Emmett St., Newark, N. J.	Apr. 3, 1902
Gilchrist, Peter S.	Chemical Engineer, Charlotte, N. C.	Apr. 3, 1902
Ginder, W. H. H.	American Sheet Steel Co., Vandergrift, Pa.	Apr. 3, 1902
Gladson, Prof. W.N.	Electrical Engineering Dpt., University of Arkansas, Fayetteville, Ark.	Apr. 3, 1902
Goddard, Chris. M.	National Board of Fire Underwriters, 55 Kilby St., Boston, Res. 1008 Beacon St., Newton Centre, Mass.	Apr. 3, 1902
Goldsborough, W. E.	Chief of Electricity Department, World's Fair, St. Louis, Mo.; Res. Lafayette, Ind.	Nov. 6, 1902
Goodrich, C. C.	Assistant General Superintendent, The B. F. Goodrich Co., Akron, Ohio.	Apr. 3, 1902

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		Date of election.*
Goodwin, H. M., Ph.D.	Massachusetts Institute of Technology, Boston, Mass.	Apr. 3, 1902
Goodwin, W. L. Ph.D.	Director School of Mining, Kingston, Ont., Can.	Apr. 3, 1902
Gordon, Prof. C. McC.	Central University of Kentucky, Danville, Ky.	Apr. 3, 1902
Granbery, J. H.	561 Walnut St., Elizabeth, N. J.	Apr. 3, 1902
Granja, Rafael	Chemical Engineer, President Ceres Chemical Co., Kingston, N. Y., Box 799.	Apr. 3, 1902
Greenstreet, C. J.	Chemist, Pittsburgh Plate Glass Co., Ford City, Pa.	Nov. 6, 1902
Gruner, Henry E.	Civil Engineer, The Laufenburger Wasserkraft Gewinnung, 9 Nauenstrasse, Basel, Switzerland.	July 3, 1902
Haber, Prof. Fritz, Ph.D.	Technische Hochschule, Karlsruhe, Germany.	Nov. 6, 1902
Hadley, A. N.	Box 33, Indianapolis, Ind.	Apr. 3, 1902
Haff, Max M.	Chemist, United Barium Co., Res. 124 Sixth St., P. O. Box 340, Niagara Falls, N. Y.	Oct. 2, 1902
Haggott, Ernest A.	Manager Arizona Blue Bell Copper Co., Mayer, Ariz.	Apr. 3, 1902
Hall, Charles M.	Pittsburgh Reduction Co., Res. 136 Buffalo Ave., Niagara Falls, N. Y.	Apr. 3, 1902
Hambuechen, Carl, E.E.	Electrochemist, 616 Lake St., Madison, Wis.	Apr. 3, 1902
Hamilton, Louis P.	Dunbar, Pa.	Apr. 3, 1902
Hance, Anthony M.	Hance Bros. & White, Philadelphia, Pa.	Apr. 3, 1902
Hanchett, Geo. T.	Electrical and Mechanical Engineer, 116 Nassau St., New York.	Apr. 3, 1902
Harper, Dr. Henry Winston	University of Texas, Res. Cor. 23rd and San Antonio Sts., Austin, Tex.	Apr. 3, 1902
Harrington, Edwin I., M.D.	100 N. Broadway, Yonkers, N. Y.	Apr. 3, 1902
Harris, Joseph W.	Ashbourne, Montgomery Co., Pa.	Apr. 3, 1902
Harris, W. D.	3609 Ludlow St., Philadelphia, Pa.	Apr. 3, 1902
Hart, Ed., Ph.D.	Professor of Chemistry, Lafayette College, Easton, Pa.	Aug. 7, 1902
Hart, Walter H.	2010 Wallace St., Philadelphia, Pa.	Apr. 3, 1902

* Members of date April 3, 1902, are charter members.

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		Date of election.*
Harvey, E. F.	St. John's, Newfoundland.	Apr. 3, 1902
Haskell, F. W.	President The Carborundum Co., Niagara Falls, N. Y.	Apr. 3, 1902
Haslwanter, Chas.	908 Willoughby Ave., Brooklyn, N. Y.	Apr. 3, 1902
Hatzel, J. C.	114 Fifth Ave., New York.	Apr. 3, 1902
Hay, Arthur M.	4041 Walnut St., Philadelphia, Pa.	Apr. 3, 1902
Heath, H. E.	Eddy Electric Mfg. Co., Windsor, Conn.	Apr. 3, 1902
Heckman, J. Conrad	Larkin Soap Mfg. Co., Buffalo, N. Y.	Apr. 3, 1902
Herbert, C. G.	Mechanical Engineer, The Solvay Process Co., Res. 815 Fort St., Detroit, Mich.	Oct. 2, 1902
Hering, Carl	929 Chestnut St., Philadelphia, Pa.	Apr. 3, 1902
Herzog, F. Benedict	Herzog Teleseme Co., 51 W. 24th St., New York.	Apr. 3, 1902
Higgins, Aldus C., C.S.	Norton Emery Wheel Co., Worcester, Mass.	Sep. 4, 1902
Hitchcock, Hal. K.	Experimental Engineer, The Pittsburgh Plate Glass Co., Floreffe, Pa.	Oct. 2, 1902
Hobbs, Perry L., Ph.D.	Western Reserve Medical College, Cor. Erie and St. Clair Sts., Cleveland, Ohio.	Apr. 3, 1902
Hofmann, Ottokar	Southwest Chemical Co., Argentine, Kans.	Apr. 3, 1902
Holman, G. U. G	Canadian Electric Light and Power Co., Ltd., 83 Dalhousie St., Quebec, Can.	Apr. 3, 1902
Hopkins, Prof. Nevil Monroe	Columbian University, 1730 I St., N. W., Washington, D. C.	Apr. 3, 1902
Hoskins, Wm.	81 S. Clark St., Chicago, Ill., Res. La Grange, Ill.	Apr. 3, 1902
Houston, Edwin J., Ph.D.	1809 Spring Garden St., Philadelphia, Pa., office 1203 Crozier Bldg.	Oct. 2, 1902
Howard, Alonzo B.	Vice-President and Treasurer Merrimac Chemical Co., 77 Broad St., Boston, Mass.	Apr. 3, 1902
Howard, Henry	175 Mountfort St., Brookline, Mass.	Apr. 3, 1902
Howard, Geo. M.	Electric Storage Battery Co., Res. 2220 Venango St., Philadelphia, Pa.	Apr. 3, 1902
Howard, Prof. S. F.	Department of Chemistry, Massachusetts Agricultural College, Res. 66 Pleasant St., Amherst, Mass.	Apr. 3, 1902

* Members of date April 3, 1902, are charter members.

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		Date of election.*
Howe, Henry M., A.M.	27 W. 73rd St., New York, Professor of Metallurgy, Columbia University.	Apr. 3, 1902
Huddle, Prof. W. J.	Western Storage Battery Co., Res. 2225 Bellefontaine St., Indianapolis, Ind.	Apr. 3, 1902
Hunt, A. M.	Consulting Engineer, 331 Pine St., San Francisco, Cal.	Apr. 3, 1902
Hunter, Thomas G.	1716 N. Broad St., Philadelphia, Pa.	Apr. 3, 1902
Hutchinson, Edw. J.	Vice-President Taylor Chemical Co., 1245 E. 3rd St., Cincinnati, Ohio.	Apr. 3, 1902
Hutchinson, Rowland W., Jr.	Eatontown, Ga.	Apr. 3, 1902
Hutton, R. S., M.Sc.	Lecturer on Electrochemistry, Owens College, Manchester, Eng.	Apr. 3, 1902
Ihlder, J. D., M.E.	Electrical Engineer, Yonkers, N. Y.	Apr. 3, 1902
Irvine, H. A.	Oldbury Electro-Chemical Co., Niagara Falls, N. Y.	Apr. 3, 1902
Isaacs, A. S., Ph.M.	Pennsylvania Malleable Co., KcKees Rocks, Pa., Res. 1214 Sheffield St., Allegheny, Pa.	Apr. 3, 1902
Isakovics, Alois von	Herbene Scientific Laboratories, 449 E. 121st St., New York.	Apr. 3, 1902
Jackson, Dugald C.	Consulting Engineer, Professor of Electrical Engineering, University of Wisconsin, Madison, Wis.	Apr. 3, 1902
Jackson, John Price, B.S., E.E., M.E.	Professor of Electrical Engineering, State College, Pa.	Oct. 2, 1902
James, J. H.	Lake Superior Power Co., Sault Ste. Marie, Ont., Can.	Apr. 3, 1902
Jenks, W. J.	120 Broadway, N. Y.	Apr. 3, 1902
Jeppson, George N.	Norton Emery Wheel Co., Worcester, Mass.	Sep. 4, 1902
Johnson, F. C.	Chemist, National Adic Co., 714 Union St., New Orleans, La.	Apr. 3, 1902
Johnson, Woolsey Mc.A.	Orford Copper Co., New Brighton, Staten Island, New York.	Apr. 3, 1902
Johnston, Thomas J.	Counsellor-at-Law, 66 Broadway, Res. 228 Willoughby Ave., New York.	Apr. 3, 1902
Jones, L. J. W.	American Smelting and Refining Co., Omaha, Neb.	Apr. 3, 1902
Kahlbaum, Prof. Geo., Ph.D.	Basel, Switzerland.	Apr. 3, 1902

* Members of date April 3, 1902, are charter members.

Digitized by Google

		Date of election.*
Kahlenberg, Louis, Ph.D.	Professor of Physical Chemistry, University of Wisconsin, Res. 306 Lake St., Madison, Wis.	Apr. 3, 1902
Keith, Dr. N. S.	Electro-Metallurgist and Mining Engineer, Room 505, 95 Liberty St., New York.	Apr. 3, 1902
Keller, Edward	P. O. Box 724, Baltimore, Md.	Apr. 3, 1902
Kelley, J. F., Ph.D.	Stanley Electric Mfg. Co., 284 W. Housatonic St., Pittsfield, Mass.	Apr. 3, 1902
Kenan, Wm. R., Jr.	Assistant Manager Traders Paper Co., Lockport, N. Y.	Apr. 3, 1902
Kennelly, Arthur E.	Professor of Electrical Engineering, Pierce Hall, Harvard University, Cambridge, Mass.	Nov. 6, 1902
Kenyon, Wm. H.	49 Wall St., New York.	Apr. 3, 1902
Kintner, C. J.	Solicitor of Patents, 45 Broadway, New York.	Apr. 3, 1902
Kitsee, Dr. Isador	306 Stock Exchange Place, Philadelphia, Pa.	Apr. 3, 1902
Klipstein, Ernest C.	122 Pearl St., New York, P. O. Box 2833, Res. 116 Prospect St., East Orange, N. J.	Apr. 3, 1902
Knapp, Geo. O	Vice-President Union Carbide Co., Res. 157 Michigan Ave., Chicago, Ill.	Nov. 6, 1902
Knox, W. J.	Care of George Westinghouse, Pittsburgh, Pa.	Apr. 3, 1902
Knudson, A. A.	Electrical Engineer, 34 Nassau St., Res. 758 Putnam Ave., Brooklyn, N. Y.	Nov. 6, 1902
Kohl, Herbert C.	Craigsville, Va.	Apr. 3, 1902
Krebbs, A. Sonnin	Krebs Pigment and Chemical Co., Newport, Del., Res., 806 Franklin St., Wilmington, Del.	Apr. 3, 1902
Kyle, T. D.	106 E. 5th St., Leadville, Colo.	Apr. 3, 1902
Lacey, Frank H.	518 Columbus Ave., Boston, Mass.	Apr. 3, 1902
Lafore, J. A.	Keystone Electric Co., Erie, Pa.	Apr. 3, 1902
Langley, John W., Ph.D.	Case School of Applied Science, Res. 77 Cornell St., Cleveland, O.	Apr. 3, 1902
Langton, John	Consulting Engineer, 72 Trinity Place, New York.	Apr. 3, 1902

* Members of date April 3, 1902, are charter members.

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		Date of election.*
Larchar, Arthur B.	Penobscot Chemical Fibre Co., Great Works, Me.	Apr. 3, 1902
Lathwood, Arthur	Chemist, Oldbury Electro-Chemical Co., Box 238, Niagara Falls, N. Y., Res. La Salle, Niagara Falls, N. Y.	Aug. 7, 1902
Laughlin, W. C.	Assayer, Chemist and Mining Engineer, Ouray, Colo., Box 1117.	Apr. 3, 1902
Leavitt, E. D.	2 Central Square, Cambridge, Mass.	Apr. 3, 1902
Lee, F. V. T.	Electrical Engineer, Vice-President and General Manager John. Martin & Co., Electrical Contractors and Engineers, 31 and 33 New Montgomery St., San Francisco, Cal.	Apr. 3, 1902
Lee, Waldemar	Chemist, Palmerton, Carbon Co., Pa.	Apr. 3, 1902
Lenher, Vic., Ph.D.	148 W. Gorham St., Madison, Wis.	Apr. 3, 1902
Levine, Edmund J.	The Fibroid Co., 636-638 Broadway, New York.	Apr. 3, 1902
Lichthardt, G	1800 M St., Box 510, Sacramento, Cal.	Apr. 3, 1902
Lincoln, A. T., Ph.D.	Instructor in Chemistry, University of Illinois, Urbana, Ill.	Nov. 6, 1902
Lincoln, P. M.	Westinghouse Electric and Manufacturing Co., Pittsburgh, Pa.	Apr. 3, 1902
Lloyd, M. G., Ph.D.	National Bureau of Standards, Washington, D. C.	Apr. 3, 1902
Lockwood, Chas. E.	439 E. 144th St., New York.	Apr. 3, 1902
Loeb, Morris	118 W. 72nd St., New York.	Apr. 3, 1902
Long, Frederick H.	Consulting Metallurgical and Contracting Engineer, 84 Adams St., Res. 2110 Clarendon Ave., Chicago, Ill.	Apr. 3, 1902
Loomis, Prof. E. H.	Princeton, N. J.	Apr. 3, 1902
Lorenz, Prof. Richard, Ph.D.	V. Moussonstrasse, Zurich, Switzerland.	Sep. 4, 1902
Lovejoy, D. R. B.S., E.E.	Electrical Engineer, Superintendent Atmospheric Products Co., Niagara Falls, N. Y.	Apr. 3, 1902
Lyman, James	Assistant Engineer, General Electric Co., Monadnock Building, Chicago, Ill.	Apr. 3, 1902
Lyndon, Lamar	Consulting Electrical Engineer, Park Row Building, Res. 243 W. 98th St., New York.	Apr. 3, 1902
MacFadden, C. K.	Geneva, Ind.	Apr. 3, 1902

* Members of date April 3, 1902, are charter members.

Digitized by Google

		Date of election.*
MacMahon, James	Castner Electrolytic Alkali Co., Superintendent Bleaching Powder Department, Niagara Falls, N. Y.	Aug. 7, 1902
MacNutt, Barry, E.E., M.S.	Physical Laboratory Lehigh University, Res. 27 S. Linden St., Bethlehem, Pa.	Apr. 3, 1902
Macomber, Irwin J.	Professor Electrical Engineering Armour Institute, Chicago, Ill.	Apr. 3, 1902
Magnus, Benj., E.E.,	Assistant Superintendent Electrolytic Refinery and Silver Mill of the Anaconda Copper Mining Co., Res. Montana Hotel, Anaconda, Mont.	Apr. 3, 1902
Mailloux, C. O.	76 William St., New York.	Apr. 3, 1902
Main, Wm.	Engineer and Chemist, 299 Jefferson Ave., Brooklyn, N. Y.	Apr. 3, 1902
Marks, Prof. W. D.	The Art Club, Philadelphia, Pa.	Apr. 3, 1902
Mathews, Wm. O.	The National Carbon Co., Dover Bay, Ohio.	Nov. 6, 1902
Marvin, A. B., Jr.	Patent Office, Washington, D. C.	Apr. 3, 1902
Mauran, Max	Engineer and Assistant Manager Castner Electrolytic Alkali Co., Niagara Falls, N. Y.	Nov. 6, 1902
Maynard, Geo. W.	20 Nassau St., New York.	Apr. 3, 1902
Maywald, Fred. J.	Chemist, 80 Broad St., New York, Res. 1028 72nd St., Brooklyn, N. Y.	Apr. 3, 1902
McConnell, Jacob Y.	500 Broad St., Philadelphia, Pa., Res. Colwyn, Pa.,	Apr. 3, 1902
McCoy, J. C.	Raritan Copper Works, Perth Amboy, N. J.	Apr. 3, 1902
McCoy, W. Asa	Raritan Copper Works, Res. 57 Kearney St., Perth Amboy, N. J.	Apr. 3, 1902
McKeown, W. W., Jr.	829 Wick Ave., Youngstown, O.	Apr. 3, 1902
McKittrick, F. J. A.	Engineer, Power and Mining Department General Electric Co., Schenectady, N. Y.	Nov. 6, 1902
Melcher, Arthur C.	58 Bowen St., Newton Centre, Private Assistant to Dr. W. R. Whitney, Massachusetts Institute of Technology, Boston, Mass.	July 3, 1902
Merz, Chas. H.	Consulting Engineer, 28 Victoria St., Westminster, London, S. W., and 1 Mosley St., Newcastle-upon-Tyne, Eng.	Apr. 3, 1902

* Members of date April 3, 1902, are charter members.

Digitized by Google

		Date of election.*
Metz, H. A.	122 Hudson St., New York.	Apr. 3, 1902
Miller, Dr. W. Lash	University of Toronto, Res. 50 St. Albans St., Toronto, Can.	Apr. 3, 1902
Molera, E. J.	Civil Engineer, 606 Clay St., San Francisco, Cal.	Apr. 3, 1902
Monell, A.	President, International Nickel Co., 74 Broadway, New York.	Apr. 3, 1902
Morgan, J. L. R., Ph.D.	Columbia University, New York.	Apr. 3, 1902
Morris, Henry G.	408 Bourse Building, Philadelphia, Pa.	Apr. 3, 1902
Morrison, Edwin	Continental Manufacturing Co., Addingham, Delaware Co., Pa.	Apr. 3, 1902
Morrison, W. J., Jr., M.S.	60-62 Broadway, New York, Res. Ridgefield Park, N. J.	Apr. 3, 1902
Moses, Herbert B.	National Battery Co., 366-382 Massachusetts Ave., Buffalo, N. Y.	Apr. 3, 1902
Mullin, E. H.	General Electric Co., 44 Broad St., New York.	Apr. 3, 1902
Murphy, Edwin J.	The British Thomson-Houston Co., Ltd., Rugby, Eng.	Oct. 2, 1902
Nichols, W. Standish	Westinghouse Electric and Manufacturing Co., Pittsburgh, Res. 835 Rebecca Ave., Wilkinsburg, Pa.	Apr. 3, 1902
Norden, Konrad, Ph.D.	169 E. 64th St., New York.	Apr. 3, 1902
Norman, Geo. M.	General Chemical Co., 517 Cooper St., Camden, N. J.	Apr. 3, 1902
Nunn, Dr. Richard J.	5 York St. E., Savannah, Ga.	Apr. 3, 1902
Oliver, Frank M.	Chemist, H. K. Mulford Co., 755 N. 38th St., Philadelphia, Pa.	Apr. 3, 1902
Osborne, Loyall A.	Westinghouse Electric and Manufacturing Co., Pittsburgh, Pa.	Apr. 3, 1902
Osterberg, Max, E.E., A.M.	Consulting Electrical and Mechanical Engineer, 11 Broadway, New York.	Apr. 3, 1902
Palmer, Prof. Chase	Professor of Chemistry, Central University of Kentucky, Danville, Ky.	Apr. 3, 1902
Palmer, E. Carlton, D.D.S.	1311 N. Broad St., Philadelphia, Pa.	Apr. 3, 1902
Parsons, Louis A., Ph.D.	Johns Hopkins University, Baltimore, Md.	Apr. 3, 1902
Patch, Maurice B.	1 Austin St., Buffalo, N. Y.	Apr. 3, 1902

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		Date of election.*
Pattee, Prof. E. N.	Syracuse University, Syracuse, N. Y.	Apr. 3, 1902
Patten, Harrison E., Ph.D.	Instructor in General Chemistry, Chemical Laboratory, University of Wisconsin, Res. 1109 University Ave., Madison, Wis.	Apr. 3, 1902
Patterson, Geo. W., Jr., Ph.D.	Junior Professor of Electrical Engineering, University of Michigan, Res. 814 S. University Ave., Ann Arbor, Mich.	Nov. 6, 1902
Pattison, Frank A.	Consulting Engineer, 141 Broadway, New York.	Apr. 3, 1902
Paul, Henry N., Jr.	929 Chestnut St., Philadelphia, Pa.	Apr. 3, 1902
Pease, Harold C.	Engineer, General Electric Co., Res. 820 Union St., Schenectady, N. Y.	Nov. 6, 1902
Pepper, David, Jr., M.E.	Contracting Engineer, Pepper & Register, 112 N. Broad St., Res. 1826 Spruce St., Philadelphia, Pa.	July 3, 1902
Perkin, Frederick Mollwo, Ph.D.	Professor of Chemistry, Borough Polytechnic Institute, Forest Hill, London, S. E., Eng.	Sep. 4, 1902
Perkins, Frank C.	Electrical Engineer, 126 Erie County Bank Building, Buffalo, N. Y.	Apr. 3, 1902
Perry, R. S.	5104 Pulaski Ave., Germantown, Philadelphia, Pa.	Apr. 3, 1902
Petty, Walter M.	Consulting Electrician, Superintendent Fire Alarm, 160 Orient Way, Rutherford, N. J.	Apr. 3, 1902
Peyton, W. C.	Martinez, Contra Costa Co., California.	Apr. 3, 1902
Pickering, Oscar W.	Teacher of Chemistry, Massachusetts Institute of Technology, Res. 52 Clifton St., Melrose Highlands, Mass., also 100 Canal St., Cleveland, Ohio.	Oct. 2, 1902
Piltschikoff, Prof. Nicolas	Professor of Physics, Technological Institute, Kharkov, Russia.	Sep. 4, 1902
Pinkerton, Andrew	Electrician American Sheet Steel Co., Vandergrift, Pa., Box 19.	Apr. 3, 1902
Pond, G. G., Ph.D.	Professor of Chemistry, State College, Pa.	July 3, 1902
Poole, Cecil P.	Editor American Electrician, 114 Liberty St., New York.	Apr. 3, 1902
Porter, John L.	Laboratory of Sewerage and Water Board, 602 Carondelet St., Res. 1317 Henry Clay Ave., New Orleans, La.	Apr. 3, 1902

* Members of date April 3, 1902, are charter members.

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		Date of election.*
Potter, Henry Noel	510 W. 23rd St., New York, Res. Rochelle Park, New Rochelle, N. Y.	Apr. 3, 1902
Powell, Thomas H.	South Norwalk, Conn.	Apr. 3, 1902
Pratt, Frederick S.	Stone and Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Price, Edgar F.	Manager Union Carbide Co., Niagara Falls, N. Y.	July 3, 1902
Rau, Prof. Albert G.	Superintendent Moravian Parochial School, Bethlehem, Pa.	Apr. 3, 1902
Reber, Samuel	Lieutenant-Colonel and Military Secretary, Headquarters of the Army, Washington, D. C.	Apr. 3, 1902
Reckhart, D. W.	Cor. San Francisco and Chihuahua Sts., El Paso, Tex.	Apr. 3, 1902
Recklinghousen, M. von, Ph.D.	11 E. 24th St., New York.	Apr. 3, 1902
Reed, C. J.	3313 N. 16th St., Philadelphia, Pa.	Apr. 3, 1902
Reed, Mrs. M. J.	3313 N. 16th St., Philadelphia, Pa.	Oct. 2, 1902
Reuterdahl, Arvid	Reuterdahl Electric Co., 67-71 Fountain St., Providence, R. I.	Apr. 3, 1902
Reynolds, F. G.	368 St. Nicholas Ave., New York.	Apr. 3, 1902
Rhodin, B. E. F.	Chief Engineer, Canadian Electro-Chemical Co., Ltd., Sault Ste. Marie, Ont., Can.	Apr. 3, 1902
Richards, Jos. W., Ph.D.	Lehigh University, Bethlehem, Pa.	Apr. 3, 1902
Riddell, D. F., Ph.C., B.Sc.	Sioux Falls College, Sioux Falls, S. Dak.	Apr. 3, 1902
Ries, Elias E.	Consulting Electrical Engineer, 116 Nassau St., New York.	Apr. 3, 1902
Roberts, Isaiah L.	Director Roberts Chemical Co., 40 Wall St., New York.	Oct. 2, 1902
Roberts, J. C.	Treasurer Atmospheric Products Co., 53 Gluck Building, Niagara Falls, N. Y.	Oct. 2, 1902
Robbins, W. A.	535 Bailey St., Camden, N. J.	Apr. 3, 1902
Robinson, Almon	P. O. Box 54, Lewiston, Me.	Apr. 3, 1902
Rochlitz, Prof. Oscar A.	Armour Institute of Technology, 623 Haddon Ave., Chicago, Ill.	Apr. 3, 1902

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		Date of election.*
Rodgers, Ashmead G.	Assistant Superintendent The Carborundum Co., Niagara Falls, N. Y.	Nov. 6, 1902
Rodman, Hugh	Electric Storage Battery Co., 19th and Allegheny Ave., Philadelphia, Pa.	Apr. 3, 1902
Roeber, E. F., Ph.D.	929 Chestnut St., Philadelphia, Pa.	Apr. 3, 1902
Roepper, C. W.	133 Phil-Ellena St., Germantown, Philadelphia, Pa.	Apr. 3, 1902
Roller, F. W.	Electrical Instruments (Machado & Roller), 203 Broadway, New York.	Apr. 3, 1902
Roller, H. C.	The Port Chester Chemical Co., Port Chester, N. Y.	Apr. 3, 1902
Rollins, Wm.	250 Marlborough St., Boston, Mass.	Apr. 3, 1902
Rosebrugh, Prof. T. R.	School of Practical Science, Toronto, Can.	Apr. 3, 1902
Rosendale, O. M.	Consulting Metallurgist, Mining Engineer, 515-516 Oregonian Building, Portland, Ore.	Apr. 3, 1902
Ross, G. McM.	Virginia City, Nev.	Apr. 3, 1902
Rossi, A. J.	35 Broadway, New York.	Apr. 3, 1902
Rowland, Lewis G.	Wetherill Separating Co., Clover and Ferguson Sts., Newark, N. J., Res. 130 N. Maple Ave., East Orange, N. J.	Apr. 3, 1902
Rowland, Arthur J.	Professor of Electrical Engineering, Drexel Institute, Res. 4510 Osage Ave., Philadelphia, Pa.	Apr. 3, 1902
Russell, Chas. J.	General Superintendent Suburban Electric Co., 4510 Frankford Ave., Philadelphia, Pa.	Apr. 3, 1902
Rushmore, David B.	Stanley Electric Manufacturing Co., Pittsfield, Mass.	Apr. 3, 1902
Ruthenberg, Marcus	1716 N. Broad St., Philadelphia, Pa., Balton House, Harrisburg, Pa., Pennsylvania Steel Co., Lebanon, Pa.	Apr. 3, 1902
Sadtler, Samuel P., Ph.D.	N. E. Cor. 10th and Chestnut Sts., Philadelphia, Pa.	Apr. 3, 1902
Sadtler, Samuel S.	N. E. Cor. 10th and Chestnut Sts., Philadelphia, Pa.	Apr. 3, 1902
Salom, Pedro G.	408 Bourse Building, Philadelphia, Pa.	Apr. 3, 1902
Saunders, Prof. A. P.	Hamilton College, Clinton, N. Y.	Apr. 3, 1902
Saunders, Lewis E., B.Sc.	Chemical Engineer, The United Barium Co., Niagara Falls, N. Y.	Oct. 2, 1902

* Members of date April 3, 1902, are charter members.

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		Date of election.*
Schlesinger, Bart. E.	The Merrimack Chemical Co., Res. 92 Mt. Vernon St., Boston, Mass.	Nov. 6, 1902
Schoonmaker, H.	917 Race St., Cincinnati, Ohio.	Apr. 3, 1902
Schreiter, Henry	Counsellor-at-Law, 20 Nassau St., New York.	Apr. 3, 1902
Seward, Geo. O.	The Wilson Aluminum Co., Holcomb Rock, Va.	Apr. 3, 1902
Shattuck, A. F.	The Solvay Process Co., Detroit, Mich.	Apr. 3, 1902
Shaw, Edwin C.	The B. F. Goodrich Co., Akron, Ohio, Res. 104 Park St.	Apr. 3, 1902
Shaw, Howard B.	Professor of Electrical Engineering, University of Missouri, Columbia, Mo.	Apr. 3, 1902
Sheldon, Samuel, A.M., Ph.D,	Professor of Physics and Electrical Engineering Polytechnic Institute, Brooklyn, N. Y.	Apr. 3, 1902
Shepherd, E. S.	205 Hazen St., Ithaca, N. Y., Res. Remington, Ind.	Apr. 3, 1902
Shorey, Edmund C.	1802 King St., P. O. Box 360, Honolulu, Hawaiian Islands.	Apr. 3, 1902
Skinner, Hervey J.	15 Chestnut St., Wakefield, Mass.	Apr. 3, 1902
Smith, Prof. A. W.	Case School of Applied Science, Res. 1101 E. Madison Ave., Cleveland, Ohio.	Apr. 3, 1902
Smith, Edmund S.	The Carborundum Co., Niagara Falls, N. Y.	Apr. 3, 1902
Smith, Edward W.	Electric Storage Battery Co., 19th St. and Allegheny Ave., Res. 5317 Germantown Ave., Philadelphia, Pa.	Apr. 3, 1902
Smith, Wm. Lincoln	Concord, Mass.	Apr. 3, 1902
Snelling, W. O.	Columbian University, Res. 1313 New York Ave., N. W., Washington, D. C.	Oct. 2, 1902
Speiden, Clement C.	Summit, N. J.	Nov. 6, 1902
Sperry, Elmer A.	National Battery Co., 366-382 Massachusetts Ave., Buffalo, N. Y.	Apr. 3, 1902
Stalnaker, E. S.	Thomas, W. Va.	Apr. 3, 1902
Steere, Thomas E., A.B.	Castner Electrolytic Alkali Co., Niagara, Falls, N. Y.	Aug. 7, 1902
Steinmetz, Chas. P.	General Electric Co., Schenectady, N. Y.	Aug. 7, 1902
Steinmetz, Jos. A.	Janney and Steinmetz Co., 826 Drexel Building, Philadelphia, Pa.	Apr. 3, 1902

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		Date of election.*
Stone, Chas. A.	Stone & Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Sweet, H. N.	50 Beacon St., Boston, Mass.	Apr. 3, 1902
Taggart, Walter T.	Instructor in Organic Chemistry, University of Pennsylvania, Res. 730 N. 20th St., Philadelphia, Pa.	Nov. 6, 1902
Taylor, Edward R.	Penn Yan, N. Y.	Apr. 3, 1902
Terven, Lewis A.	75 W. Washington Place, New Yok.	Apr. 3, 1902
Tesla, N.	46 and 48 E. Houston St., New York.	Apr. 3, 1902
Thelberg, John, M.D.	45 W. 32nd St., New York.	Apr. 3, 1902
Thomas, Chas. W.	Secretary Reebel Paper and Lithograph Co., Nutley, N. J.	July 3, 1902
Thomas, J. W	Hokendauqua, Pa.	Apr. 3, 1902
Thompson, Robt. M.	President Orford Copper Co., 99 John St., New York.	Apr. 3, 1902
Tillberg, Erik W.	Chemist, Norton Emery Wheel Co., Res. 20 Green Lane, Worcester, Mass.	Nov. 6, 1902
Tone, F. J.	Superintendent The Carborundum Co., Niagara Falls, N. Y.	Apr. 3, 1902
Townsend, C. P.	918 F St., N. W., Washington, D. C.	Apr. 3, 1902
Ulke, Titus	Consolidated Lake Superior Power Co., Sault Ste. Marie, Ont., Can.	Apr. 3, 1902
Vander Naillen, A.	The A. Vander Naillen School of Engineering, 113 Fulton St., San Francisco, Cal.	Apr. 3, 1902
Vaughn, Chas. F.	Superintendent Castner Electrolytic Alkali Co., Niagara Falls, N. Y.	Nov. 6, 1902
Vincent, Jos. A.	421 Chestnut St., Philadelphia, Pa.	Apr. 3, 1902
Voege, Adolph L.	Technische Hochschule, Zurich, Switzerland.	Apr. 3, 1902
Vogel, G. C.	Pfister & Vogel, Milwaukee, Wis.	Apr. 3, 1902
Volney, C. W.	173 W. 81st St., New York.	Apr. 3, 1902
Voorhees, Louis A.	P. O. Box 357, New Brunswick, N. J.	Apr. 3, 1902
Vorce, Loren R.	Suite 29, 509 Russell Ave., Cleveland, Ohio.	Oct. 2, 1902
Wagner, Henry L., M.D., Ph.D.	Professor Laryngology, University of California, 522 Sutter St., San Francisco, Cal.	Apr. 3, 1902
Wahl, W. H., Ph.D.	Secretary Franklin Institute, 15 S. 7th St., Philadelphia, Pa.	Apr. 3, 1902

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		Date of election.*
Wainwright, J. W., M.D.	177 W. 83rd St., New York.	Apr. 3, 1902
Waite, Loren G.	1381 Boston Road, New York.	July 3, 1902
Walker, W. H., Ph.D.	Little & Walker, 19 Exchange Place, Boston, 613 Walnut St., Newtonville, Mass.	Aug. 7, 1902
Waterman, Frank N.	150 Nassau St., New York.	Apr. 3, 1902
Way, W. S.	Electrical Engineer, 106 St. Julian St. W., Savannah, Ga.	Apr. 3, 1902
Weaver, W. D.	Editor Electrical World and Engineer, 114 Liberty St., New York, Res. 55 Demarest Ave., Englewood, N. J.	Apr. 3, 1902
Webster, Edwin S.	Stone and Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Weedon, Wm. S., Ph.D.	Research Laboratory, General Electric Co., Schenectady, N. Y.	Apr. 3, 1902
Weidemann, J. E.	773 Union St., Brooklyn, N. Y.	Apr. 3, 1902
Weightman, A. T.	Electrochemist, The Electrical Lead Reduction Co., Box 253 Niagara Falls, N. Y.	Apr. 3, 1902
Weil, Samuel	Superintendent Electrical Lead Reduction Co., Niagara Falls, N. Y.	Oct. 2, 1902
Wells, Prof. J. S. C.	Columbia University, New York.	Apr. 3, 1902
Wells, J. Walter	Belleville, Ont., Can.	Apr. 3, 1902
Westman, Gustaf M.	1144 Broadway, New York.	Apr. 3, 1902
Weston, Edward	Waverly Park, N. J.	Apr. 3, 1902
White, Ray Hill, A.B.	Assistant Chemist, The United Barium Co., Niagara Falls, N. Y.	Oct. 2, 1902
Whiting, Prof. S. E.	11 Ware St., Cambridge, Mass.	Apr. 3, 1902
Whitney, C. E.	Electrical and Mechanical Engineer, 123 Liberty St., New York, Res. 553 S. 6th Ave., Mount Vernon, N. Y.	Apr. 3, 1902
Whitney, Willis R., Ph.D.	General Electric Co., Schenectady, N. Y.	Apr. 3, 1902
Whitten, Wm. M.	Pittsburgh Reduction Co., Niagara Falls, N. Y.	Apr. 3, 1902
Wiechmann, F. G. Ph.D.	P. O. Box 79, Station W., Brooklyn, N. Y.	Apr. 3, 1902
Wilbert, M.I., M.D.,	German Hospital, Philadelphia, Pa.	Apr. 3, 1902

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		Date of election.*
Wilder, Stuart	Stanley Electric Manufacturing Co., 23 E. Housatonic St., Pittsfield, Mass., Res. Knoxville, Tenn.	Apr. 3, 1902
Willyoung, Elmer G.	11 Frankfort St., New York.	Apr. 3, 1902
Witherspoon, R. A.	Superintendent The Ampere Electro-Chemical Co., Res. 170 Buffalo Ave., Niagara Falls, N. Y.	Oct. 2, 1902
Witherspoon, T. A.	Examiner, U. S. Patent Office, Washington, D. C.	Apr. 3, 1902
Wolcott, Townsend	329 Clinton St., Brooklyn, N. Y.	Apr. 3, 1902
Wood, E. F.	Vice-President International Nickel Co., P. O. Box 1325, 74 Broadway, New York.	Apr. 3, 1902
Yard, H. H.	Mining Engineer, 415 Drexel Building, Philadelphia, Pa.	Apr. 3, 1902
Yarrow, Thomas J., Jr., M.D.	1739 N. 16th St., Philadelphia, Pa.	Apr. 3, 1902
Young, W. D.	Electrical Engineer, B. & O. R. R. Co., Res. 309 Oakdale Road, Roland Park, Baltimore, Md.	Apr. 3, 1902
Zeller, Frank M.	Continental Mfg. Co., Old Stock Exchange, Philadelphia, Pa.	Apr. 3, 1902
Zimmermann, Jas. G.	Assistant in Electrochemical Laboratory, Res. 214 Brooks St., Madison, Wis.	Nov. 6, 1902

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OBITUARY.

Charles W. Kennedy; elected April 3, 1902; died September 1, 1902

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AMERICAN ELECTROCHEMICAL SOCIETY.

GEOGRAPHICAL DISTRIBUTION OF MEMBERS.

(Nov. 6, 1902.)

UNITED STATES.

ARIZONA.

Mayer.—Haggott, Ernest A.

ARKANSAS.

Fayetteville.—Gladson, Prof. W. N., University of Arkansas.

CALIFORNIA.

Martinez.—Peyton, W. C.

Sacramento.—Lichthardt, G., 1800 M St.

San Francisco.—

Allen, Wyatt H., 331 Pine St.
Arden, Henry, 900 Pine St.
Emery, Arthur L., Indiana and 24th Sts.
Hunt, A. M., 331 Pine St.
Lee, F. V. T., 31 and 33 Montgomery St.
Molera, E. J., 606 Clay St.
Vander Naillen, Prof. A., 113 Fulton St.
Wagner, Dr. Henry L., 522 Sutter St.

COLORADO.

Argo.—Fritchle, Oliver P.

Leadville.—Kyle, T. D., 106 E. 5th St.

Ouray.—Laughlin, W. C.

CONNECTICUT.

New Haven.—

Bradley, Walter M., 1346 Chapel St.

South Norwalk.—Powell, Thomas H.

Windsor.—

Eddy, A. H., Eddy Electric Manufacturing Co.
Heath, H. E., Eddy Electric Manufacturing Co.

DELAWARE.

Wilmington.—Krebs, A. S., Krebs Pigment and Chemical Co.

DISTRICT OF COLUMBIA.

Byrnes, Eugene A., 918 F. St., N. W.
Ewin, James L., 900 F St., N. W.
Frazier, Robert F., 918 F St.
Hopkins, N. M., 1730 I St., N. W.

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Lloyd, M. G., Nat. Bureau of Standards.
Marvin, A. B., Jr., Patent Office.
Reber, Samuel, Headquarters of the Army.
Snelling, O. W., 1313 New York Ave., N. W.
Townsend, C. P., 918 F St., N. W.
Witherspoon, T. A., Examiner, U. S. Patent Office.

GEORGIA.

Eatontown.—Hutchinson, R. W., Jr.

Savannah.—
Nunn, Dr. Richard J., 5 York St., East.
Way, W. S., 106 St. Julian St., West.

ILLINOIS.

Chicago.—
Askew, C. B., 1652 Monadnock Building.
Bates, Wm. S., 510 Boylston Building.
Brill, Geo. M., 1134 Marquette Building.
Freeman, C. E., Armour Institute.
Hoskins, Wm., 81 S. Clark St.
Knapp, Geo. O., 157 Michigan Ave.
Long, Frederic H., 84 Adams St.
Lyman, Jas., Monadnock Building.
Macomber, Prof. I. J., Armour Institute.
Rochlitz, Prof. Oscar A., Armour Institute.

Urbana.—
Brooks, Prof. Morgan, University of Illinois.
Lincoln, A. T., University of Ill.

INDIANA.

Bloomington.—Brown, Prof. Oliver W., Indiana University.

East Chicago.—Doggett, Chas. S.

Geneva.—MacFadden, C. K.

Indianapolis.—
Hadley, A. N., Box 33.
Huddle, Prof. W. J., 2225 Bellefontaine St.

KANSAS.

Argentine.—Hofmann, Ottokar, Southwest Chemical Co.

KENTUCKY.

Danville.—
Gordon, Prof. Clarence McC., Central University of Kentucky.
Palmer, Prof. Chase, Central University of Kentucky.

LOUISIANA.

New Orleans.—
Johnson, F. C., 714 Union St.
Porter, John L., Laboratory of Sewerage and Water Board.

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MAINE.

Cumberland Mills.—Gabriel, George A., Box 390.
Great Works.—Larchar, Arthur B., Penobscot Chemical Fibre Co.
Lewiston.—Robinson, Almon, P. O. Box 54.
Orono.—Burbank, Prof. John E., University of Maine.

MARYLAND.

Baltimore.—
Keller, Edward, P. O. Box 724.
Parsons, Louis A., Johns Hopkins University.
Young, W. D., Baltimore & Ohio Railroad Co.

MASSACHUSETTS.

Amherst.—
Howard, Prof. S. F., Massachusetts Agricultural College.
Boston.—
Amster, N. L., 32 Equitable Building.
Bleecker, John S., 93 Federal St.
Buchanan, Leonard B., 93 Federal St.
Goddard, Chris. M., 55 Kilby St.
Goodwin, Dr. H. M., Massachusetts Institute of Technology.
Howard, Alonzo P., 77 Broad St.
Lacey, Frank H., 518 Columbus Ave.
Pickering, O. W., Massachusetts Institute of Technology.
Pratt, Frederick S., 93 Federal St.
Rollins, Wm., 250 Marlborough St.
Schlesinger, Barthold E., 92 Mount Vernon St.
Stone, Chas. A., 93 Federal St.
Sweet, H. N., 50 Beacon St.
Walker, Wm. H., 19 Exchange Place.
Webster, Edwin S., 93 Federal St.
Whitney, Dr. Willis R., Massachusetts Institute of Technology.
Brookline.—
Howard, Henry, 175 Mountfort St.
Cambridge.—
Adams, Prof. C. A., Harvard University.
Adams, Isaac, 1776 Massachusetts Ave.
Kennelly, Arthur E., Harvard University.
Leavitt, E. D., 2 Central Square.
Whiting, Prof. S. E., 11 Ware St.
Concord.—Smith, Wm. Lincoln.
Dedham.—Coggeshall, G. W., Chestnut St.
Lawrence.—Alden, John.
Lynn.—Fleming, R., General Electric Co.
Newton Center.—Melcher, Arthur C., 58 Bowen St.
Pittsfield.—
Creighton, Elmer E. Farmer, Stanley Electric Manufacturing Co.
Kelley, John F., Stanley Electric Manufacturing Co.
Rushmore, David B., Stanley Electric Mfg. Co.

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Wilder, Stuart, Stanley Electric Manufacturing Co., 23 E. Housatonic St.
Quincy.—Clare, Jas. P., 51 Edison St.
Wakefield.—Skinner, Hervey J., 15 Chestnut St.
Worcester.—
Higgins, Aldus C., Norton Emery Wheel Co.
Jeppson, Geo. N., Norton Emery Wheel Co.
Tillberg, Erik W., Norton Emery Wheel Co.

MICHIGAN.

Ann Arbor.—
Carhart, Prof. H. S., University of Michigan.
Patterson, Geo. W., Jr., University of Michigan.
Detroit.—
Barnes, S. G., 310 Boulevard West.
Herbert, C. G., 815 Fort St.
Shattuck, A. F., The Solvay Process Co.
Midland.—Dow, Herbert H.
Sault Ste. Marie.—Edmands, J. R., Union Carbide Co.

MINNESOTA.

Minneapolis.—Frankforter, Prof. G. B., University of Minnesota.

MISSOURI.

Columbia.—
Brown, Prof. W. G., University of Missouri.
Shaw, Prof. H. B., University of Missouri.
St. Louis.—
Anderson, Edward L., 2700 Euclid Ave.
Goldsborough, W. E., World's Fair.

MONTANA.

Anaconda.—Magnus, Benjamin.
Helena.—Gerry, M. H., Jr., Missouri River Power Co.

NEBRASKA.

Lincoln.—Evans, Herbert S., University of Nebraska.
Omaha.—Jones, L. J. W., American Smelting and Refining Co.

NEVADA.

Virginia City.—
Fielding, F. E.
Ross, G. McM.

NEW HAMPSHIRE.

Berlin.—
Barker, E. R., Burgess Sulphite Fibre Co.
Barton, Chas. B., Burgess Sulphite Fibre Co.
Concord.—Coit, Dr. James Milnor, St. Paul's School.

NEW JERSEY.

Camden.—
Norman, Geo. M., General Chemical Co.
Robbins, W. A., 535 Bailey St.
Carteret.—Doney, D. C.

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East Orange.—Fliess, Robert A., 44 Chestnut St.
Elizabeth.—Granbery, J. H., 561 Walnut St.
Newark.—
Colby, Edward A., Baker Platinum Works.
Gifford, Wm. E., 59 Emmet St.
Rowland, L. G., Clover and Ferguson Sts.
New Brunswick.—Voorhees, Louis A., P. O. Box 357.
Nutley.—Thomas, Chas. W.
Perth Amboy.—
Addicks, Lawrence, Raritan Copper Works.
Easterbrooks, Frank D., Raritan Copper Works.
Foersterling, Dr. Hans, Roessler & Hasslacher Chemical Co.
McCoy, J. C., Raritan Copper Works.
McCoy, W. Asa, 57 Kearney Ave.
Princeton.—Loomis, Prof. E. H.
Rutherford.—Petty, Walter M.
Summit.—Speiden, Clement C.
Waverly Park.—Weston, Edward.

NEW YORK.

Auburn.—Case, Willard E.
Brooklyn.—
Fletcher, Geo. W., 38 Grove St.
Haslwanter, Chas., 908 Willoughby Ave.
Main, Wm., 299 Jefferson Ave.
Sheldon, Dr. Samuel, Polytechnic Institute.
Weidemann, J. E., 773 Union St.
Wiechmann, F. G., P. O. Box 79, Station W.
Wolcott, Townsend, 329 Clinton St.
Buffalo.—
Bierbaum, C. H., Lumen Bearing Co.
Heckman, J. Conrad, Larkin Soap Manufacturing Co.
Moses, Herbert B., 366–382 Massachusetts Ave.
Patch, Maurice B., 1 Austin St.
Perkins, Frank C., 126 Erie Co. Bank Building.
Sperry, Elmer A., 366–382 Massachusetts Ave.
Clinton.—
Saunders, Prof. A. P., Hamilton College, Clinton, N. Y.
Flatbush.—Barr, B. M., 234 E. 21st St., L. I.
Ithaca.—
Bancroft, Dr. Wilder D., Cornell University.
Carveth, Prof. Hector R., Cornell University.
Shepherd, E. S., 205 Hazen St.
Kingston.—Granja, Rafael, President Ceres Chemical Co.
Lockport.—Kenan, Wm. R., Jr.
Mount Vernon.—Blackmore, H. S.
New Brighton, S. I.—Johnson, Woolsey McA.

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New York.—

Adams, Ernest K., 455 Madison Ave.
Adams, Geoffrey C., 29 Broadway.
Atwood, Geo. F., Western Electric Co.
Austen, Dr. Peter T., 80 Broad St.
Banks, Wm. C., 439–445 E. 144th St.
Barstow, W. S., Bowling Green Offices.
Batchelor, Chas., 52 Broadway.
Block, Wesley S., 40 Wall St.
Bogue, Chas. J., 213-215 Center St.
Bowman, Walker, 39 Cortlandt St.
Bradley, Chas. S., 44 Broad St.
Brown, Harold P., 120-122 Liberty St.
Brown, J. Stanford, 489 Fifth Ave.
Browne, Wm. Hand, Jr., Park Row Building.
Caldwell, Edward, 114 Liberty St.
Cameron, Walter S., 239 W. 136th St.
Coho, H. B., 149 Broadway.
Crocker, F. B., Columbia University.
Davis, H. J., 65 Wall St.
Donaldson, Wm. W., 25 W. 33rd St.
Doremus, Dr. Charles A., 17 Lexington Ave.
Dunn, Clifford E., 13-21 Park Row.
Durant, Edward, 115 E. 26th St.
Elliot, Arthur H., 4 Irving Place.
Falding, Frederick J., 52 Broadway.
FitzGibbon, R., 77 John St.
Forbes, Francis, 34 Nassau St.
Hanchett, Geo. T., 116 Liberty St.
Hatzel, J. C., 114 5th Ave.
Herzog, F. B., 51 W. 24th St.
Howe, Henry M., Columbia University.
Isakovics, Alois von, 449 E. 121st St.
Jenks, W. J., 120 Broadway.
Johnston, Thomas J., 66 Broadway.
Keith, N. S., 95 Liberty St.
Kenyon, Wm. H., 49 Wall St.
Kintner, C. J., 45 Broadway.
Klipstein, Ernest C., 122 Pearl St., P. O. Box 2833.
Knudson, A. A., 34 Nassau St.
Langton, John, 72 Trinity Place.
Levine, Edmund J., 636-8 Broadway.
Lockwood, Chas. E., 439 E. 144th St.
Loeb, Morris, 118 W. 72nd St.
Lyndon, Lamar, Park Row Building.
Mailloux, C. O., 76 William St.
Maynard, Geo. W., 20 Nassau St.

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Maywald, F. J., 80 Broad St.
Metz, H. A., 122 Hudson St.
Monell, A., 74 Broadway.
Morgan, J. L. R., Columbia University.
Morrison, W. J., Jr., 60-62 Broadway.
Mullin, E. H., 44 Broad St.
Norden, Dr. Konrad, 169 E. 64th St.
Osterberg, Max, 11 Broadway.
Pattison, Frank A., 141 Broadway.
Poole, Cecil P., 114 Liberty St.
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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 15, 1902, President Richards in the Chair.

ON THE TESTING OF CARBON ELECTRODES.

By Francis A. J. FitzGerald.

I. DETERMINATION OF DENSITY.

In both electrochemical and electrometallurgical processes, in which carbon electrodes are used, the determination of the density of the latter is important. The general efficiency of the electrode will depend on the nature of the carbon and on the methods used in their manufacture, and much may be learned on these points by density determinations. A discussion of what may be learned from density determinations being outside the scope of the present paper, we may turn at once to the method of applying the test.

Two determinations of density should be made: (1) *Real Density;* that is, the density of the carbon of which the electrode is made, and (2) *Apparent Density;* that is, the ratio of the weight of the electrode to its volume taken as a whole. From these two quantities a third quantity, *Porosity*, may be calculated. The porosity is the ratio of the difference of the volume of the electrode taken as a whole and the volume of the carbon of which it is composed to the volume of the electrode taken as a whole, or substituting densities for volumes we have the equation:

$$\text{Porosity} = \frac{\text{Real Density} - \text{Apparent Density}}{\text{Real Density}}.$$

The determination of the real density is by no means easy because of the persistence with which amorphous carbons and graphites retain air.

One method is to boil the specimen, which has been reduced to a fine powder, in some liquid of high density; for example, methylene iodide, dilute till the carbon sinks, and then determine the density of the liquid. This method, however, is not suitable for manufacturing purposes, and after many experiments the following method was found to be the most satisfactory.

Apparatus.—A volumeter, which is a bottle with a long neck

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having an inside diameter of about 20 mm. and graduated to 100 cc. in divisions of 0.2 cc. The volumeter is fitted with a rubber stopper through which passes a glass tube. The end of the glass tube inside the volumeter is drawn to a point and bent back on itself for a reason that will appear later. A water-bath, in which the volumeter is placed to keep its contents at a constant temperature. A vacuum pump, preferably fitted with a gauge. Kerosene oil, such, for example, as "Acme Crown" kerosene which has a high flashing-point and is consequently free from the more volatile paraffines. Oil is used in the volumeter because it will readily wet carbon. A balance that will weigh accurately to 0.1 gram.

Method.—A specimen that will fit into the volumeter and that weighs at least 30 grams, is cut from the electrode and weighed. The volumeter is partly filled with kerosene and placed in the water-bath in order to keep the temperature constant throughout the experiment. A reading of the volumeter is then taken, the specimen introduced and the volumeter connected with the vacuum pump. When the vacuum gauge has shown the maximum attainable vacuum for a period of about ten minutes, the volumeter is disconnected and a reading taken, after which the operation is repeated and another reading obtained. This method is followed till two consecutive readings are the same. The difference of the last reading and the original reading is the real volume of the specimen and from this the real density may be calculated.

When the volumeter is connected to the vacuum pump, strong effervescence occurs owing to the escape of air from the electrode and this suggested a possible source of error due to the evaporation of the oil. In order to study this point, a specimen of an electrode was immersed in a known weight of oil, contained in a bottle, and the bottle and its contents weighed. The bottle was then connected with the vacuum pump and, after effervesence had ceased, was again weighed. A serious loss in weight, amounting to 2 or 3 per cent. of the original weight of the oil, was observed; but subsequent investigation showed that this was not due to evaporation, but to the drawing off of a fine spray, caused by the bursting of the air bubbles at the surface of the oil. The difficulty was overcome by drawing out and bending back on itself the end of the glass tube which was used for connecting

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the bottle with the vacuum pump, for this, to a great extent, prevented the spray from being drawn out of the apparatus.

In all the density determinations I have made by this method a filter-pump, which reduces the pressure to about 20 mm. of mercury, has been used. In order to determine if this imperfect vacuum introduced a constant error in the observations, an electrode, having a real volume of about 36 cc. was put in the volumeter and the latter connected with the filter-pump which was regulated to reduce the pressure to 105 mm. When the oil in the volumeter had reached a constant volume a reading was taken. The volumeter was then connected to the filter-pump again and a pressure of 58 mm. obtained without producing any appreciable change in the volume of the oil. Finally the pressure was reduced to 20 mm. but the reading was still the same.

Using the method described above, six determinations of the density of a graphite electrode were made. The mean of the determinations was 2.1899 and the average deviation was found to be 0.0083 or a percentage deviation of 0.38. The determination of the density of another electrode was made in the same way and it was then cut up into small pieces and a second determination made with great care, using a specific gravity bottle. The results obtained were as follows:

Density by volumeter	2.1884
Density by specific gravity bottle.....	2.1930

The results obtained show that the method is sufficiently accurate for manufacturing purposes.

The determination of the apparent density is comparatively simple, for it is merely necessary to give the electrode a light coat of shellac, put it into the volumeter, which now contains water, and observe the volume of water displaced. In determining the porosity of electrodes it is important that the real and apparent densities be determined with the same specimen, since both these quantities vary in different carbons. In examining a large electrode care must be taken to obtain an average specimen, for, because of the methods used in its manufacture, the apparent density of the electrode is not uniform throughout. This is clearly illustrated by the following experiment. Three specimens were cut from a graphite electrode having a cross-section of 51 x 178 mm. One specimen was cut from the side of the elec-

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trode in a longitudinal direction; the second was cut in the same direction, but from the center; the third was cut transversely and represented an average of the cross-section of the electrode. The densities of the three specimens were determined with the results shown in the following table:

Specimen.	Real density.	Apparent density.	Porosity.
Side	2.19	1.75	0.21
Center	2.19	1.60	0.27
Average	2.19	1 63	0.26

II. THE DETECTION OF AMORPHOUS CARBON AND GRAPHITE.

In certain electrolytic processes the use of amorphous carbon electrodes is unsatisfactory because of their rapid disintegration in the electrolyte. This may be overcome to a certain extent by special methods of manufacture or by using amorphous carbons, such as retort carbon, which show greater resistance to disintegration. Similar remarks apply to the use of carbon electrodes for the electric furnace in metallurgical work. Of all forms of carbon, graphite shows the greatest resistance to oxidizing and disintegrating actions; when, therefore, it is possible to use carbon at all, graphite gives the best results. It is obvious, however, that an electrode made like the ordinary graphite brush, such as is frequently used on dynamos and motors, would be of little use, since the graphite particles are held together by a binding material of amorphous carbon and consequently disintegration would be nearly if not quite as rapid as in the use of amorphous carbon electrodes. To obtain the best possible results the electrode should contain no amorphous carbon, and is therefore important to have some method of testing electrodes to determine whether they are composed entirely of graphite.

M. Berthelot first described a method of separating the different forms of carbon by submitting them to the oxidizing action of a mixture of nitric acid and potassium chlorate.[1] In applying this test the best results are obtained by using anhydrous nitric acid and potassium chlorate that has been thoroughly dried at a temperature of about 150°. About 0.5 gram of the finely powdered electrode is introduced into a test-tube, containing 10 cc. of nitric acid, and to this is added cautiously 4 grams of potassium chlorate. The test-tube is then placed in a water-bath and kept at a tem-

[1] Ann. chim. phys., [4], 19, 392.

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perature of 60° till all action is over, that is, for about ten to twelve hours. The nitric acid is then poured off, the residue thoroughly washed with hot water by decantation and dried. By repeatedly treating the specimen in this way all the amorphous carbon present is converted into a yellowish brown, soluble substance, while the graphite yields a yellow, insoluble solid which has been named graphitic oxide by Berthelot. Where a mixture of graphite and amorphous carbon is under examination, the presence of the latter is readily recognized by the reddish brown color of the water used in washing the oxidized products. The wash-water from the oxidized products of amorphous and graphitic carbon, respectively, is shown in these two test-tubes. Both amorphous carbons and graphites vary greatly in the ease with which they are attacked by the oxidizing mixture, some carbons requiring many more treatments than others before the oxidation is complete, and this gives us a method of comparing their relative resistance to disintegrating actions.

The eight test-tubes shown here illustrate a test on an electrode ; test-tube 0 contains a specimen from an electrode made of Acheson graphite ; test-tube 1, the dark green substance obtained after the first treatment with the oxidizing mixture ; test-tube 2, the residue after the second treatment—its color is now a lighter green ; and so on with the other test-tubes, till we come to test-tube 7 containing the substance obtained after seven treatments ; this is a pale yellow graphitic oxide. When the conversion into graphitic oxide is complete, further treatment with the oxidizing mixture produces no change. Graphitic oxide may be readily recognized by its peculiar property of decomposing with deflagration when heated, yielding an intensely black, flocculent substance, named pyrographitic oxide by Berthelot. When pyrographitic oxide is treated with the oxidizing mixture it is completely destroyed, leaving a clear solution. This tube contains a specimen of pyrographitic oxide obtained by heating some of the graphitic oxide in test-tube 7.

In oxidizing the specimen from the Acheson graphite electrode, none of the brown colored substance was obtained, indicating, therefore, the entire absence of amorphous carbon and that the electrode consists wholly of graphite. In the next test-tube is a specimen of the substance obtained when amorphous carbon is treated twice with the oxidizing mixture. This specimen

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actually contains a trace of graphite, but in order to find this, it would be necessary to continue the oxidation till all the amorphous carbon had been removed, when yellow graphitic oxide would remain as a measure of the amount of graphite present.

When it is desired to test an electrode to determine whether it is composed wholly of amorphous carbon or whether it contains a certain amount of graphite, a method due to Staudenmaier may be used.[1] The specimen is treated once with the oxidizing mixture, washed, heated on the water-bath with a solution of potassium permanganate and sulphuric acid, and finally treated with an excess of hydrogen peroxide. If the specimen consists wholly of amorphous carbon, a clear solution of a reddish brown color is obtained, but if any graphite is present there remains an insoluble residue of a yellow or greenish yellow color. To illustrate this test, specimens were taken from two electrodes, one of graphite, the other of amorphous carbon, and treated as described above. The products obtained are shown in these two test-tubes, the graphite electrode being identified by the insoluble, yellow residue.

DISCUSSION.

DR. EDWARD HART: Mr. President, while I was listening to Mr. FitzGerald's paper it occurred to me that possibly ammonium persulphate might be used in this connection for distinguishing between amorphous and graphitic carbon. I do not know whether it is generally known, but a method has recently been devised by which the persulphates are used in the determination of manganese. It has been found that when persulphates are heated with a substance containing manganese with the addition of a little nitrate of silver, that permanganic acid is formed, and this process has been used in some laboratories to displace the old method altogether. Quite a large quantity of ammonium persulphate is now used. I do not know whether it has occurred to Mr. FitzGerald to try that.

PROF. R. S. HUTTON: Mr. Chairman, I should like to ask if any experiments have been made upon graphites prepared in different ways, and the behavior of such graphites towards

[1] J. Soc. Chem. Ind., (1898), p. 880.

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chemical reagents and also as electrodes. Moissan, in preparing graphite in many different ways, principally by dissolving carbon in different metals, I understand obtained very different forms of graphite according to the metal to which he used as solvent of the carbon. It seems to me that such experiments, if they have been carried out, might throw light on the behavior of different compounds in causing this change of carbon into graphite, and possibly might even tend to show in what way one might obtain an improvement of the Acheson graphite, which is already very perfect as a form of carbon for electrode purposes. But it seems to me one could easily produce these different forms of graphite, preparing them from such solutions in metals, and compare their behavior towards the gases evolved in electrolysis. Such results might give interesting indications as to the best oxide to mix with the carbon in producing electrodes for any particular purpose.

DR. N. S. KEITH: I know that, in the electrolysis of copper solutions, using graphitic carbon made by the Acheson Graphite Company, solutions have been obtained of a similar color. I will not say they are exactly of the same constitution. I have not tested them in respect to that. After some considerable length of time, attended by some considerable disintegration of the carbon, I have filtered the solution, deposited the copper and other metals therefrom, and then obtained a solution like that in color. I have not gone any further as to a test of other characteristics.

MR. F. A. J. FITZGERALD: Mr. President, I was much interested in Professor Hart's suggestion of the use of persulphates for determining or detecting amorphous carbon in graphites. I confess that I am ignorant of the method, but am glad Professor Hart has mentioned it and I hope to be able to test it shortly. As regards Mr. Hutton's question, Professor Moissan, in his experiments, found that there were as many different kinds of graphite as there were of amorphous carbon, and the experiments made at the International Acheson Graphite Company's laboratory has confirmed this. For example, graphites vary greatly, according to the metal used, when Moissan's method of "different solubilities" is used. The subject, however, is such a large one that it would be impossible to discuss it at present. Incidentally I may mention, however, that in making graphitic oxide, certain graphites are completely converted in about three treatments, while others take seven and sometimes ten. There can be no doubt

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that different graphites exhibit different degrees of resistance to oxidizing actions, and this is just one of the many differences that are found in both natural and artificial graphites. As regards the brown solution obtained when Acheson graphite electrodes are used in the electrolysis of copper solution, I have found similarly colored solution formed when sulphuric acid is electrolyzed, using these electrodes. I cannot say what the cause of this coloring is, but it may be due to the formation of these peculiar solid oxides of carbon.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 15, 1902, Vice-President Doremus in the Chair.

THE EFFICIENCY OF ELECTRIC FURNACES.

By Joseph W. Richards.

An electric furnace is a furnace for accomplishing a physical or chemical change in materials by means of the agency of heat, said heat being supplied by the transformation of electric energy. The change or effect on the materials treated being due to the heating, the output of the furnace or the capacity, as measured by amount of material treated and amount of product obtained, will be more or less proportional to the amount of heat energy developed in the furnace. I say "*more* or *less* proportional" because, although the amount of heat necessary to produce the change in a given amount of material may be a perfectly definite quantity, yet the proportion of the heat developed in the furnace which is actually absorbed or applied in producing this change is a variable one, being always less than 100 per cent., and frequently very much less. The proportion of the heat energy of the electric current thus applied to producing the useful physical, or physical and chemical, change in the charge, is what I term the *efficiency* of the furnace.

The usefully applied heat will include one or both of two factors. The first factor is, the amount of heat necessary to heat the charge up to the temperature of the furnace. This is a physical change, and is found by taking into consideration the items of the charge, their specific heats in the solid state, also their specific heats in the liquid state and their latent heats of fusion, if they are melted, and the temperature to which they are heated. We thus obtain the quantity of heat necessary to bring them, and thence the whole charge, up to the working temperature of the furnace. My friends who are fond of mathematical expressions can easily put this proposition into the shape of a simple formula, but the matter will be easily understood as expressed above. In some electric furnace operations this is the only result aimed at, and the ratio of this amount of heat to that

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generated by the conversion of the electric current into heat energy, will be the useful effect or *efficiency* of the operation. The second factor, which appears in many, and in fact, in the majority of cases, is the heat absorbed in chemical reactions between the constituents of the charge when they are heated to the reacting point, which is the temperature of the furnace. This is a thermo-chemical question. The physical state which conditions a chemical reaction is usually *fluidity*, coupled with opportunity for gaseous products of the reaction to escape from the sphere of reaction as soon as they are formed. This is a condition analogous to the insolubility of a possible product in a solution, which factor usually conditions a chemical reaction in solution by removing from the sphere of reaction the least trace of the new product as soon as formed, and therefore causing its formation to continue if there is the slightest predisposing tendency to its production. The reactions thus brought about in the charge in electric furnace operations are usually heat-absorbing reactions, and the heat thus absorbed must be supplied by the furnace, that is, taken from the energy of the current. This amount must then be added to the heat required to bring the charge up to its reacting temperature, and the sum constitutes the usefully applied heat, and its ratio to the whole heat energy of the current is what I would term the *efficiency* of the furnace.

The degree of efficiency thus attainable depends on many factors, a partial enumeration of which is: size of the furnace, temperature of the reaction, protection from radiation, management of the terminals, feeding and tapping, general management. Of these, by far the most important, in commercial practice, is the size of the furnace. Large bodies cool much more slowly than small ones, and this is because their radiating surface, by which they lose heat, is *proportionately* so much smaller. A suspended cube of any material, one meter on its edge, has one cubic meter volume to six square meters radiating surface; if one decimeter on its edge, it has one liter volume to six square decimeters radiating surface. That is, for one-thousandth the volume it has one-hundredth the radiating surface. Expressing it the other way, the larger cube has only one-tenth the radiating surface of the smaller one *per unit of volume or contents*. It follows that if the two cubes are heated to the same temperature, the larger one will lose only one-tenth as much heat in a given differential of

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time, per unit of contents, as the smaller one. If, therefore, it is wished to operate a furnace at a given fixed temperature, the loss by radiation is reduced very greatly by increasing the size of the furnace and the scale of the operation. The capacity or contents of the furnace increases approximately as the cube of the linear dimensions; the radiating surface, conditioning the loss of heat, increases as the square of the linear dimensions; therefore the proportion of radiating surface to unit of contents *decreases* approximately in proportion as the linear dimensions are increased. Make a circular furnace of twice the diameter and twice the height, its cubic capacity is increased eight times, and its radiating surface four times, and if eight times the current energy is used there will be approximately only half as much percentage loss by radiation in the larger furnace. This consideration alone would indicate the probability that if a 100 horse-power electric furnace was working at an efficiency of 50 per cent. with the other 50 per cent. lost by radiation and conduction, that an 800 horse-power furnace of the same design working the same process at the same temperature, should lose only 25 per cent. and give an efficiency nearer to 75 per cent. Indeed, it is quite conceivable that at the limit, a change from working a furnace process from the smallest practicable scale to the largest practicable scale, might convert an operation working at 10 per cent. efficiency and 90 per cent. loss into an operation of 90 per cent. efficiency and 10 per cent. loss. Along with the increased size, where possible, comes also, in general, greater uniformity of working, regulation of temperature and control of the process, so that most of the *desiderata* of commercial success lie in the direction of increasing the size of the furnaces to the furthest limit set by mechanical or physical considerations.

Dr. Borchers has classified electric furnaces into the resistance type and the arc type, the former being subdivided into those in which the material to be heated is heated by its own resistance, or by the resistance of a contiguous conductor, the latter being subdivided into those in which the charge is fed directly into the arc or is heated by radiation from the arc. For the purposes of our calculations of *efficiency*, however, we will classify the operations according to the nature of the change brought about in the charge, and therefore distinguish, first, operations in which the charge undergoes simply a physical change, and second those in

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which the change is both physical and chemical. The first class would include those in which the charge is simply heated without melting as well as those in which it is fused; the second would include those in which *chemical* change takes place without melting the charge, or with a fusion of the same. As types of these four classes we might mention, in their order, the graphitization of carbon, the melting of alumina, the production of carborundum, the production of barium oxide.

Siemens tried to introduce on a commercial scale the electrical fusion of steel by an electric arc. He has stated that the results he obtained on an experimental scale showed 50 per cent. of the heat energy of the current to have been utilized. This was, however, on a small scale, using but 2 horse-power, and a greater efficiency would certainly have been attained working on a larger scale. This class of operations however, as we will see later, seem to give a higher efficiency than those in which chemical changes supervene.

HEATING ALONE WITHOUT FUSION.

As example of this we will take the conversion of anthracite coal into graphite, in the Acheson furnaces. It is true that some chemical changes probably occur during the conversion, such as the progressive formation and decomposition of carbides, but these are negligible because of their plus and minus heat quantities neutralizing each other; the change from amorphous carbon to graphite is a heat-*evolving* reaction, and therefore must be reckoned as really *assisting* the current, or practically, diminishing in our figuring the calculated efficiency.

The data are as follows: 1000 horse-power in twenty hours, converts 12,000 pounds of anthracite into 10,000 pounds of graphite. Assumed temperature of the furnace 3300° C.; specific heat of coal to that temperature 0.5; heat of conversion 236.5 calories per pound of graphite formed.

N. B. [For convenience we will use *pound calories* (per 1° C.), as giving all the figures needed for our calculations of efficiency without transposing the data.]

Heat equivalent of the current: 20,000 cal. per minute = 24,000,000 cal. per twenty hours.

Heat used in heating charge: $12{,}000 \times 0.5 \times 3{,}300 = 19{,}800{,}000$ cal. = 82.5 per cent.

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Heat gained in conversion into graphite: 10,000 × 236.5 = 2,365,000 cal., or an amount equal numercially to 10 per cent. of the heat supplied by the current.

Heat lost by radiation and conduction: 100 — 82.5 = 17.5 per cent. of the heating power of the current.

Efficiency: The real amount of heat available was 100 + 10 = 110 per cent. of the heating power of the current. Of this, 82.5 per cent. was utilized, giving an efficiency of 82.5 ÷ 110 = **75** per cent.

In the Acheson process of graphitizing electrodes by placing them crosswise embedded in a resistant material, a considerably smaller proportion of the energy goes into the articles being graphitized because the resistance material has also to be heated to the temperature of graphitization. In this case, the actual heat furnished to the carbons being graphitized is approximately half of the total heat absorbed by the charge, and only 38 per cent. of the total heat available.

Data: 1000 horse-power graphitizes 7,000 pounds of electrodes embedded in 7,000 pounds of granular carbon and lining.

Energy of current: 28,800,000 pound calories.

Heat in electrodes: 7,000 × 0.5 × 3,300 = 11,550,000 calories.

Heat of conversion: 7,000 × 236.5 = 1,655,500 calories.

Total heat available: 30,455,000 calories.

Net efficiency of operation $\frac{11,550,000}{30,455,000}$ = **38** per cent. applied to useful purpose.

HEATING ALONE, WITH FUSION.

The Jacobs' process of fusing calcined bauxite is an illustration The process is simple fusion by the arc in a cylindrical pot.

Energy of current: 215 horse-power for fourteen hours = 3,612,000 pound calories per run.

Heat in charge: the heat in liquid alumina has not been determined experimentally. From a consideration of the heat in liquid slags and the temperature of the furnace it is thought that 880 pound calories per pound of liquid alumina is a probable value. This would make the heat in 3,000 pounds of charge 2,640,000 calories = **74** per cent. of the total energy available.

HEATING AND CHEMICAL CHANGE, WITHOUT FUSION.

The manufacture of carborundum is a good example. A

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mixture of carbon, silica sand and salt is heated by the incandescence of a conducting carbon core, until the salt is volatilized, carrying off most of the metallic impurities as chlorides; the silica is reduced and combines with the excess of carbon present to form silicon carbide. The furnace is 20 feet long, and 1,000 horse-power of current is passed through for thirty-six hours.

Charge.			
1,000	pounds	carbon	in core.
7,200	"	"	" charge.
12,000	"	silica	" "
3,000	"	salt	" "
7,000	"	silicon carbide formed.	

Assumptions: temperature of furnace 3000° C.; specific heat of carbon 0.5, of silica 0.25, of salt 0.2. Heat of formation of silica = 200,000 calories (per 60 pounds), of carbonic oxide 29,000 calories (per 28 pounds), of silicon carbide small but positive, and assumed as 2,000 calories (per 40 pounds). It is further assumed that only the part of the charge actually reduced is heated to the full temperature of the furnace, and the heat going into the unreduced material or packing is not included in the *efficiency*. Reaction assumed:

$$3C + SiO_2 = CSi + 2CO.$$

Heat energy of current: 1,000 horse-power for thirty-six hours = 45,620,000 pound calories.

Heat absorbed in heating up part of charge reduced or volatilized: 7,300 pounds of carbon = $7,300 \times 0.5 \times 3,000 = 10,950,000$ calories; 10,500 pounds of silica = $10,500 \times 0.25 \times 3,000 = 7,875,000$ pound calories; in salt volatilized $3,000 \times 50 = 150,000$ calories. Total 18,975,000 calories = 42 per cent. of energy of current.

Heat absorbed in chemical reactions: the heat required to split up one molecular weight (60 pounds) of silica is 200,000 calories; the formation of one molecular weight of silicon carbide and two molecular weights of carbonic oxide gives us 60,000 calories, leaving a deficit of 140,000 calories per molecular weight of carbide formed (40 pounds), or 3,500 calories per pound of carbide, or 24,500,000 calories for the total 7,000 pounds of carbide = 53.5 per cent. of the total energy of the current. This value is too high, and the reason is that the heats of formation

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we have used are those at ordinary temperature, while the reaction takes place at a high temperature with the absorption of less heat. How much less heat is absorbed may be determined by the following considerations. The amount calculated is the theoretical absorption at ordinary temperatures. It takes 42 per cent. of the energy of the current to heat the charge up to the reacting temperature, and yet the products of the reaction, silicon carbide and carbonic oxide, contain much less than that amount of energy as sensible heat; the difference between the heat required to bring the charge up to the reacting temperature and the sensible heat in the products of the reaction at the same temperature, represents the quantity by which the heat absorbed in the chemical reaction has diminished, owing to the higher temperature at which it takes place. Now, the heat in 7,000 pounds of silicon carbide is about $7,000 \times 0.3 \times 3,000 = 6,300,000$ calories; in the 9,800 pounds of carbonic oxide 2,200,000 calories, giving a total heat in the products of 8,500,000 calories. Since it took 18,975,000 calories to heat up the charge, the difference, 10,475,000 calories, has disappeared, and has gone towards furthering the chemical reaction. The chemical reaction has therefore absorbed from outside $24,500,000 - 10,475,000 = 14,025,000$ calories $= 34.5$ per cent. of the energy of the current.

Efficiency: heating up charge, 42 per cent. + 34.5 per cent. absorbed in the chemical reaction = **76.5** per cent. net efficiency.

HEATING WITH FUSION AND CHEMICAL REACTION.

There are numerous instances of this kind of electric furnace operations, in which, particularly, reductions to metal or other metallic compounds are operated. The United Barium Co.'s process is a good instance, barium sulphate being mixed with a small amount of carbon and the charge reduced to a mixture of barium sulphide and oxide in the electric furnace. The calculations, however, are complicated by the fact that the chemical reaction absorbs very much less heat at the furnace temperature than that calculated at the ordinary temperature, as is known from the fact that the efficiency calculated without reference to that factor runs over 100 per cent. The specific heat of the product is unknown, as well as its composition being variable, so that it is impossible at present to allow for the correction required.

The production of calcium carbide presents some interesting

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data, and may be employed to illustrate this class of operations. Assuming an output of 4 tons per 1,000 horse-power per day, or 250 horse-power days per ton, the temperature 2750° C., and using the heats of formation at ordinary temperature, we have.

Heat energy of current: 250 horse-power per day = 7,200,000 pound calories.

Absorbed in heating charge: 2,000 pounds of lime = 2,000 × 0.25 × 2,750 = 1,375,000 calories; 1,500 pounds of coke = 1,500 × 0.5 × 2,750 = 2,062,500. Sum, 3,437,500 calories.

Absorbed in chemical reaction: In the formation of 64 parts of carbide, the heat balance is as follows:

Decomposition of 56 parts of lime	—130,500 cal.
Formation of 64 parts of carbide	— 7,250 "
Heat absorbed	—137,750 "
Formation of 28 parts carbonic oxide	29,400 "
Net heat absorption	—108,350 "
Absorbed per unit of carbide	1,690 "
Absorbed per ton of carbide	3,380,000 "

This figure may be too high, like that calculated for formation of carborundum, but we do not have the data to make further corrections. The sum total of the heat required to heat up the charge and that absorbed in chemical reactions is 6,817,500 calories, or nearly 95 per cent., which is certainly too high. An assumption of a probable value for the specific heat of the carbide would change the figures materially, making the heat absorbed in the reaction only 14 per cent. of the whole heating effect, which added to the 48 per cent. required to heat up the charge gives a net efficiency of 62 per cent.

There is a distinct experimental gap in the lack of knowledge of the specific heat of these products of the electric furnace, at high temperatures. When these are known, our calculations can be made with much greater exactness.

The net result, however, seems to point to a commercial efficiency of 60 to 75 per cent. calculating, as I have indicated, with furnaces of 200 to 1,000 horse-power. The value of such an approximate figure is, that any one starting an electric furnace operation should be able to calculate the approximate output to be expected; or, if planning or designing for a given output, will have a guide to indicate the approximate size and capacity of the furnaces needed.

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I have left out of consideration the cases where electrolysis takes place, using fused electrolytes, because in these the production is proportional to the amperes of current used, and not to the total energy of the current, and can be operated only with direct current. Such are essentially strictly electrolytic processes, in which the heating effect of the current is unavoidable and incidental to the main process of electrolysis, and such must be excluded from the term "electric furnace processes" if that term is to retain its individuality and stand for a definite class of operations.

The considerations of such electrolytic operations on fused salts may be carried out in a similar manner to the above calculations, using the energy absorbed in the electrolytic decomposition and secondary reactions as energy rendered latent and utilized. I have worked out, as an example, the electrolysis of fused sodium chloride by the Acker process as follows:

8,200 amperes are passed through a pot electrolyzing 36.5 pounds of sodium chloride per hour. The drop of potential is 6.5 volts, of which 3.5 are absorbed in electrolytic decomposition. We can therefore say at once, that $\frac{3.5}{6.5} = 54$ per cent. of the energy of the current is usefully applied to decomposition of the electrolyte. In addition to this 36.5 pounds of salt must be melted per hour. The whole energy of the current, 8,200 amperes by 6.5 volts drop, is equal to 85,300 pound calories per hour. The salt requires the following heat, per pound to melt it and bring it to 850°:

To bring to melting-point 775°, 0.25×775	= 143.5 cal.
Latent heat of fusion	= 40.0 "
To bring up to 850°, $0.3 \times (850-775)$	= 22.5 "
Total per pound of salt	= 206.0 "
" " 36.5 pounds of salt	= 7,519 cal.

This quantity is therefore $\frac{7,519}{85,300} = 9$ per cent. of the total heat energy of the current.

Efficiency: the sum of 9 and 54 gives 63 per cent. of the energy of the current usefully applied; the other 37 per cent. is lost by radiation. Of the total heat actually generated by the resistance of the electrolyte, $9 \times \frac{6.5}{3} = 19.5$ per cent. is absorbed in melting the freshly added salt, and 80.5 per cent. is lost by radiation and in the hot products.

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DISCUSSION.

MR. CARL HERING: Mr. Chairman, I am glad that Professor Richards has called attention to this important term, efficiency, because it seems to me that it is often used very loosely, and unless there is an explanation of what is meant by the term in any particular case, the figures will mean absolutely nothing, or almost nothing, because the term efficiency can be applied to various stages of the process. The proper meaning of efficiency is the actual divided by the theoretical amount of energy, but the trouble with furnaces is that frequently we do not know what the theoretical amount is. In many cases it has not been determined, and in other cases it has been determined only roughly. I believe I am correct in saying that for calcium carbide the actual figure is not yet definitely known, unless it has been determined very recently. There is another way in which the efficiency of a furnace can be stated, in which it is perfectly safe to use the term, namely, to say that the efficiency of a certain furnace is so and so many pounds of the final product per kilowatt hour. This is, perhaps, a loose way of using the term efficiency, but it is a practical way, and whenever the theoretical figures are not known, it seems to me that it affords a very good way of stating the efficiency of furnaces when you want to compare different ones for doing the same work. This use of the term is analogous to its use in connection with incandescent lamps; there also we do not know the theoretical light equivalent, so we speak of the efficiency of an incandescent light as being so and so many candles per watt, or watts per candle.

Much can often be learned if we analyze the efficiencies of various parts of the process in a furnace. In many cases heat is actually absorbed in the formation of the compound, as for instance in the formation of calcium carbide heat is absorbed, so to speak; that is, energy is being stored up in the final product. This is a very important factor in calculating efficiencies.

There is one term in connection with the measurements of the efficiency of certain furnaces which it is very difficult to include because one cannot measure or calculate it. It occurs in resistance furnaces in which the current passes through the material itself, and is due to the loss by the conduction of current through the lining of the trough, which is generally fire-brick. It is

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known that fire-brick at a certain temperature will conduct current; that this is a leakage current which causes no electrolysis of the compound, but merely supplies heat; the trouble is, that one cannot measure or calculate the amount.

PROF. W. D. BANCROFT: If I understood Professor Richards rightly, it appears that he counts in the heat of fusion in making his calculations in regard to efficiency. Now, the heat of fusion, of course, is a factor in considering the length of time necessary for the furnace to heat up to the equilibrium temperature under a given current, but it does not seem to me that it has anything to do with the final temperature that has been reached, because that final temperature is simply a question of the actual radiation at that temperature; the mass is fused, and the amount of heat necessary to fuse it does not come in in determining the equilibrium temperature.

PROF. HART: Mr. Chairman, I would like to call attention to one fact. We start out in the application of electric energy with a tremendous handicap, where it is not made, as here, by water-power. In many cases it cannot be made by water-power. Take nitric acid: it is impossible to transport nitric acid cheaply a long distance. It is necessary, therefore, to make it on the spot. You cannot get the water-power, for example, in Pittsburg, and there you start in with a tremendous handicap. This is a question which will well bear very thorough investigation, because upon the successful utilization of collectible energy where a high percentage of the energy is obtained, largely depends the future of electricity.

MR. WHITNEY: Mr. Chairman, I should like to learn, if possible, what experiments have been made to reduce this loss of approximately forty per cent. of the energy, which, as I understand it, is the loss through radiation, as I am interested in knowing how much that may possibly be reduced by building the retaining walls of the furnace in such a way as to leave small air chambers throughout the wall.

DR. HABER: I am interested in learning what numbers you use for the output of calcium carbide; what number of kilowatt-hours do you use in the calculations per ton of carbide produced?

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PROF. RICHARDS: I would say in reply to Mr. Hering, that the term efficiency has two meanings, according to whether it is a continuous operation, or a discontinuous one. That is, it may have two shades of meaning. In a continuous operation it represents the melting of the substance added and that absorbed in chemical decomposition. The relation of those two factors to the total would be the efficiency. In a discontinuous operation like the manufacture of graphite, you have simply the heating-up of the material to the final temperature. What heat is radiated after the operation stops, in a discontinuous operation, I would account as heat which had been usefully applied, and not as radiated heat that is totally lost, whereas in a continuous operation all that is lost by radiation is a total loss.

In the manufacture of calcium carbide I have taken a production of four tons per day per thousand horse-power as the basis of my calculation.

With regard to the loss in the lining of the furnace, that was illustrated in the loss in the packing around articles to be graphitized. For instance, the current is passed through the articles to be graphitized, but they must be covered up with a heat insulating material in order to bring them up to a proper temperature, and the lining of the furnace, if the packing may be so-called, in that case absorbed, I think, 30 per cent. of the energy of the current. But in the case of the current passing through the substance itself, and not through the lining, as in the case of a non-conducting lining, that amount, I think, is usually small. The conductivity of the charge increases greatly with the high temperature, more rapidly than the conductivity of the lining, which is not heated to so high a temperature, and the ratio of the current going through the charge to that going through the lining is, in my experience, large. In one furnace on which I made experiments and calculations, 96 per cent. of the current went through the charge material, while only 4 per cent. went through the lining of the furnace. In regard to Professor Bancroft's remark about the heat of fusion in the continuous operation, for instance, in the Acker process, where salt is continually added in solid form, it has to be heated, melted, and brought up to the temperature of the furnace, and its latent heat of fusion as well as its specific heat in the solid and liquid stages, will have to be brought into

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the calculation in order to get the total heat used for liquefying the materials charged.

The idea has often come to me, as to an electric furnace, to look at it as if it were Pegasus hitched to a cart. You have a source of very intense and high temperature, but you can keep that temperature down by regulating the supply of materials, and the temperature can be kept within moderate limits by a rapid charging and discharging of materials from the furnace; so that it is quite possible to conduct an electric operation at ordinary furnace temperature, keeping it down by simply putting a load on it; that is, by charging and discharging the furnace rapidly. I think that principle can be made use of with very fruitful results in chemical operations which we want to take place at a comparatively low temperature.

Replying to Mr. Whitney, I have no experience with regard to making walls hollow or attempting to reduce the radiation in that way. I think the increase of the size of the furnace, where practicable, is the far better way of decreasing relatively the amount of radiation, increasing the size of the furnace and the rate at which the furnace works, and you thus decrease relatively very rapidly the amount of heat lost by radiation. It is like working a steel furnace fast or slow. By working a furnace fast you can reduce the relative amount of loss by radiation and increase the efficiency very greatly.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 15, 1902, President Richards in the Chair.

CATHODIC REDUCTION.

By ALFRED T. WEIGHTMAN.

The effect of the reducing action of a current at the cathode can show itself in two distinct ways, I. by the reduction of the ions in the solution or, II. by reduction of the electrode itself. It is the latter of these reactions which it is now proposed to discuss, but before doing so a general consideration of the first case will be necessary. Numerous examples of this could be taken, almost every case of the deposition of metals coming under this head, and it is too well known to dwell upon further here. The matter, however, becomes a little more complicated when two electrolytes are in solution of which it is possible to liberate both negative or both positive ions simultaneously, and the various conditions which will influence the composition of the liberated ions, and the relation which the amount of each liberated ion bears to the number of ions which are in solution, has been the subject of much study.

It is, of course, principally influenced by the heat equation of the two reactions, that which absorbs the least enérgy taking place more readily, and the greater the difference in energy absorption the greater will be the difference of the relative proportions of the liberated ions. It is also influenced by the concentration of the two electrolytes and indirectly by the current density. For instance, take the case of a mixed solution of $ZnCl_2$ and $CuCl_2$. The heat of formation is respectively 113,000 cal. and 62,500 cal. and, consequently, although the conduction through the solution takes place by all the ions present, the copper will be deposited far more easily than the zinc and, in fact, the zinc will not be deposited at all until a very large difference in the concentration of the Cu and Zn ions is reached. For two electrolytes whose heats of formation are closer, the difference in concentration for both ions to be liberated will be proportionately smaller. This can be easily deduced from Nernst's equation,

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which applies equally well to the electromotive force of polarization of an electrolytic cell as to the electromotive force of a voltaic cell. From this equation it can be easily seen that, in the case of mixed electrolytes, C (the concentration) may be so proportioned for each electrolyte that the electromotive force of the polarization is the same for both, but the extent to which these must differ will be mainly dependent on E_0 (electromotive force of the cell for normal solution), which in turn is dependent on the nature of the liberated ions.

The current density affects it indirectly by impoverishing the solution of the more easily liberated ion at the surface of the electrode quicker than diffusion can take place and bring it back to the same composition as the bulk of the solution. If the heats of formation are closer together, as in the case of Hg and Ag, they will be deposited almost in proportion to the percentages of each present in the solution.

After this brief résumé of reduction from the solution we now come on to the second case, where the reducing action of the current acts upon the cathode itself. In this case the cathode is usually a compound of a metal, and either by the reducing action of the current or by the action of nascent hydrogen, which ever way you are pleased to look at it, the H ions combine with the non-metallic radical forming a new compound. The reduction of AgCl to Ag, as in the De la Rue standard cell, is a case in point, but probably the most familiar one is that of the negative plate of a storage cell where, during charge, the insoluble $PbSO_4$ is reduced to the metallic condition.

We have here two possible cathode substances, namely, $PbSO_4$, which under the reducing action of the current will yield Pb and H_2SO_4, and the metallic lead, either in the form of a grid or spongy lead from previously reduced sulphate, which will, of course, evolve H. With two possible cathodes present we have, of course, two possible reactions which can take place simultaneously, namely, the reduction of $PbSO_4$ or the evolution of H, and the proportion in which these cathodes are present will influence the relative distribution of the current between the two reactions.

The principal conditions, however, which will determine this are, or at least should be, the heat equation of those two reactions, as was seen to be the case in reduction from the solution.

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The following are the two thermochemical equations of these reactions:

$$PbSO_4 + H_2O = PbO + H_2SO_4\ aq = 23{,}400 \text{ cal.}$$
$$PbO = Pb + O = 50{,}300 \text{ "}$$
$$73{,}700 \text{ "} \qquad (1)$$
$$H_2SO_4\ aq = H_2SO_4\ aq + H_2 + O = 68{,}360 \qquad (2)$$

It will be seen that the reduction of $PbSO_4$ requires a slightly higher voltage than the liberation of H. It is an astonishing thing therefore that more H is not evolved from a negative plate during charge than is actually found to be the case. As a matter of fact very little H is evolved until the extreme end of the charge is reached when practically all the $PbSO_4$ has been reduced. This is still more extraordinary when higher current densities are used. In the case of a storage battery, on raising the current density the liberation of H increases, although this is the reaction which requires the least energy absorption. From the consideration of reduction from solution, on raising the current density the reaction requiring the *greater* energy absorption increases. Of course, I quite realize that in the latter case, as the ions undergoing reduction are in solution, diffusion comes into account while in the former case it does not, but it is still rather unlooked for that the amount of H should actually increase.

In the Salom process for the production of lead sponge, at present worked by the Electrical Lead Reduction Company at Niagara Falls, the reactions are similar to those above described for the negative plate of a storage cell with this difference: PbS (in the form of native galena) is used instead of $PbSO_4$, with the production of H_2S instead of H_2SO_4. But on considering the heat equation of the two possible reactions they are found to lie even farther apart than in the case of the reduction of the sulphate just considered, still more favoring the production of H in preference to the reduction of the lead compound. The following thermochemical equations clearly show this:

$$PbS = Pb + S = -20{,}400 \text{ cal.}$$
$$S + H_2 = H_2S = +\ 4{,}510 \text{ "}$$
$$H_2O = H_2 + O = -68{,}360 \text{ "}$$
$$-84{,}250 \text{ "} \qquad (1)$$
$$H_2SO_4\ aq = H_2 + O + H_2SO_4\ aq = 68{,}360 \text{ cal.} \qquad (2)$$

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The heat of solution of H_2S does not come into account excepting right at the start, as the solution is quickly saturated. In fact, in most of the experiments to be hereafter described the solution was saturated with H_2S from an outside source before hand, so as to eliminate any variations this might bring about.

The difference is so great that at first sight it appears to be an almost impossible problem to reduce the sulphide without having an enormous waste of current spent in the liberation of H, which is, of course, from the point of view of the manufacturer, an undesirable reaction and merely represents so much waste of current. I have conducted a very large number of experiments at the works of the Electrical Lead Reduction Company, with a view to producing as small an evolution of H as possible, or in other words, raising the current efficiency as high as possible so as to reduce the largest quantity of PbS for a given current. The efficiency is extremely sensitive to: (1) Degree of purity of ore and the nature of those impurities; (2) Conductivity of ore; (3) Fineness of grinding; (4) Strength and purity of electrolyte; (5) Thickness of layers of ore; (6) Temperature of solution, and various other causes; but strange to say, is almost uneffected by current density. Of course, the first essential point for the reduction of an electrode is that it should be an electrical conductor. When the electrical resistance of the ore is spoken of it must not be inferred that pure PbS in the mass is of variable conductivity, but impurities present influence it very considerably. The grinding also effects it, the principle source of resistance not being so much in the ore itself as in the resistance at the points of contact between the particles of ore, which is an extremely variable quantity. By finer grinding the number of points of contact is increased and the resistance is correspondingly raised. The electrical resistance of pure PbS is given by J. Guinchant as 0.000298 at 0° C., increasing almost proportionately to 0.01294 at 920° C.

Ores as obtained direct from the mine differ considerably in their electrical conductivity, and this is a property of lead ore which miners are not usually called upon to consider.

All sorts of variations were at first obtained due to neglect of these conditions, and it would be tedious to go through the influence all these various properties have upon the efficiency of the reduction, but a few results given under the most favorable con-

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ditions and in the most perfect form of the process may be of interest.

By analyzing the gases evolved from a reduction it is possible to tell what proportion of the current is being used in depriving the ore of sulphur and what proportion is being used in liberating hydrogen.

For the purpose of ascertaining the progress satisfactorily it was found to be important to keep the gases from the anode and cathode separate, for reasons to be explained later. The gases from the cathode were collected at intervals during reduction and a sample of the more or less reduced ore removed. These were then analyzed, the gases for their percentages of H and H_2S and the ore for Pb and PbS. Plotting time as abscissae and the percentages of H_2S as ordinates we obtain a curve showing the composition of the liberated gases at any moment. Again plotting time as abscissae and the percentages of PbS as ordinates we obtain a curve showing the composition of the ore at any moment. Some interesting comparisons can then be made showing how the composition of the ore will influence the composition of the gases. The following tables I, II, III and IV, and curves Figs. 1, 2, 3 and 4 give the results obtained for various current densities.

TABLE I.

Current, 2.4 amps. Ore, 28 grams PbS.

Time in minutes.	Gases.		Ore.	
	H, per cent. by volume.	H_2S, per cent. by volume.	Pb, molecular percentage.	PbS, molecular percentage.
15	52.8	47.2	4.3	95.7
20	35.2	64.8	6.3	93.7
30	22.4	77.6	11.0	89.0
40	18.4	81.6	16.1	83.9
50	13.6	86.4	21.4	78.6
60	12.8	87.2	26.7	73.3
100	13.6	86.4	47.9	52.1
120	16.0	84.0	58.2	41.8
140	19.2	80.8	68.2	31 8
160	24.4	75.6	77.4	22.6
180	34.4	65.6	85.5	14.5
200	51.0	49.0	91.5	8.5
220	77.6	22.4	94.2	5.8
240	89.6	10.4	95.5	4.5
260	93.6	6.4	96.3	3.7
280	95.2	4.8	96.5	3.5

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TABLE II.

Current, 3.6 amps. Ore, 30 grams PbS.

Time in minutes.	Gases.		Ore.	
	H, per cent. by volume.	H_2S, per cent. by volume.	Pb, molecular percentage.	PbS, molecular percentage.
15	36.0	64.0	8.5	91.5
25	14.0	86.0	16.2	83.8
35	8.0	92.0	24.3	75.7
50	8.0	92.0	36.6	63.4
70	9.6	90.4	52.6	47.4
80	10.8	89.4	60.5	39.5
90	15.2	84.8	68.1	31.9
100	21.8	78.2	75.0	25.0
110	27.2	72.8	81.5	18.5
120	37.6	62.4	87.0	13.0
130	60.8	39.2	90.5	9.5
140	80.0	20.0	92.2	7.8
150	92.0	8.0	92.9	7.1
170	94.4	5.6	93.9	6.1
190	95.2	4.8	94.8	5.2

TABLE III.

Current, 4.8 amps. Ore, 27 grams PbS.

Time in minutes.	Gases.		Ore.	
	H, per cent. by volume.	H_2S, per cent. by volume.	Pb, molecular percentage.	PbS, molecular percentage.
5	77.0	23.0	1.5	98.5
10	41.0	59.0	5.4	94.5
15	24.8	75.2	10.5	89.5
20	15.5	84.5	16.5	83.5
25	8.0	92.0	22.5	77.5
30	6.4	94.6	28.9	71.1
35	7.2	92.8	35.0	65.0
40	7.2	92.8	41.1	58.9
45	7.2	92.8	47.4	52.6
50	7.6	92.4	53.5	46.5
60	9.6	90.4	65.5	34.5
70	20.0	80.0	76.0	24.0
75	28.8	71.2	80.8	19.2
80	45.6	54.4	84.2	15.8
85	60.0	40.0	86.9	13.1
90	72.8	27.2	88.8	11.2
95	80.0	20.0	90.0	10.0
100	84.0	16.0	91.1	8.9
110	92.4	7.6	92.0	8.0
140	94.4	5.6	94.2	5.8
160	96.0	4.0	95.2	4.8

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Fig. 1.

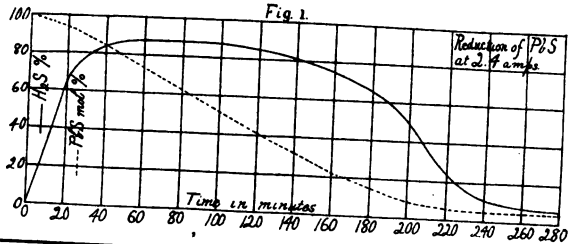


Fig. 2.

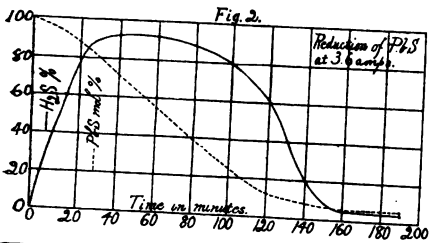


Fig. 5.

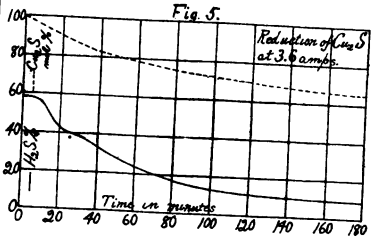


Fig. 3.

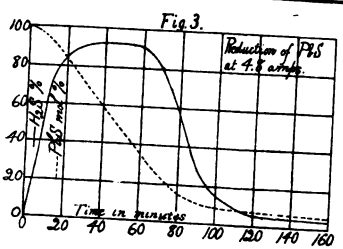


Fig. 6

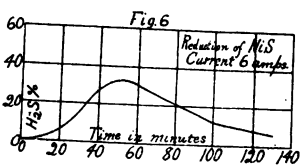
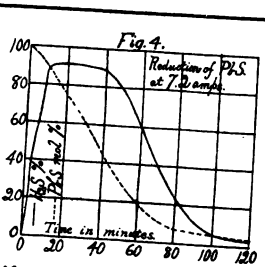


Fig. 4.



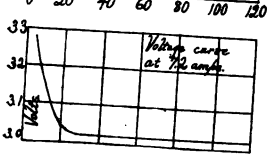


Fig. 7.

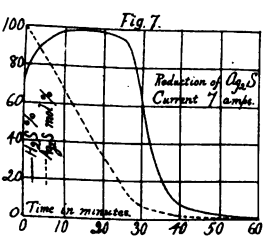


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TABLE IV.

Current, 7.2 amps. Ore, 28 grams PbS.

Time in minutes.	Gases.		Ore.		Volts.
	H, per cent. by volume.	H_2S, per cent. by volume.	Pb, molecular percentage.	PbS, molecular percentage.	
5	46.0	54.0	4.4	95.6	3.28
10	12.0	88.0	11.7	88.3	3.16
15	8.6	91.4	19.2	80.8	3.09
20	8.4	91.6	26.8	73.2	3.04
25	8.8	91.2	34.4	65.6	
30	9.2	90.8	41.9	58.1	3.01
35	9.6	90.4	49.3	50.7	
40	11.6	88.4	56.6	43.4	3.02
45	15.2	84.8	63.6	36.4	
50	22.0	78.0	70.0	30.0	3.02
55	30.4	69.6	75.8	24.2	
60	39.2	60.8	80.8	19.2	3.02
65	51.2	48.8	84.8	15.2	
70	60.8	39.2	88.0	12.0	3.01
75	69.6	30.4	90.5	9.5	
80	77.0	23.0	92.4	7.6	3.02
85	84.8	15.2	93.7	6.3	
90	90.4	9.6	94.5	5.5	3.02
100	94.8	5.2	95.3	4.7	3.02
110	96.0	4.0	95.9	4.1	3.02
120	96.8	3.2	96.5	3.5	3.02

The similarity in the shape of the curves under different current densities is remarkable, in fact, the number of ampere hours necessary for a given percentage of sponge in the ore agrees within the limits of experimental error. This was further corroborated by stopping experiments at various points in the curve and then raising and lowering the current. The composition of the evolved gases was scarcely altered by doing this. Probably this might be accounted for by the fact that diffusion does not come into account as in the case of reduction from solution.

But perhaps a more remarkable thing is that the yield of H_2S should be so high, when we refer back to the thermochemical equations previously given. It was there shown that the reaction $PbS + H_2 = Pb + H_2S$ required a very much higher absorption of energy than the mere liberation of H. And yet, under proper conditions, this reaction which, from the point of view of the process is the desirable one, can be kept up to an efficiency yield of 80 per cent., or over, for two-thirds of the reduction, even when

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the compound undergoing reduction, namely, PbS, is present to the extent of only 25 per cent. It is natural to expect that H_2S would only be evolved when the percentage of Pb was small and would not be evolved at all when the percentage of Pb had reached 20 or 30 per cent. Yet in the case under discussion with a difference of 15,890 cals. between the two possible reactions precisely the opposite effect is produced and the reaction requiring the greater absorption of energy gives as large as an 80 per cent. yield when only 25 per cent. of the reacting substance is present, in spite of the fact, too, that the reduced lead sponge is even a better electrical conductor than the PbS. Had it been the other way about, namely, that the lead sponge was of higher electrical resistance than the PbS, some explanation might be forthcoming, as more current would be carried by the latter in proportion to its superior conductivity.

The voltage curve does not tell us much, and only in one case is it given in the above experiments, as it keeps quite steady after once the contact resistance of the particles has been overcome. The actual volts given are not the actual volts required in practical work. It has been previously mentioned that it was necessary for experimental purposes to keep the gases from the anode and cathode separate and the method adopted for doing this introduced considerable resistance in the circuit which accounts for the volts per cell being so high. This, however, does not affect the relative value of the readings, that is to say, any rise or fall of volts would be noticeable, as the resistance remains constant.

The first sudden rise of the gas curve from zero to about 90 per cent. is a little mysterious, but is probably due to a comparatively high resistance of the ore at the start, as indicated by the voltage curve. The gases would then tend to be evolved from the supporting grid, which, being of sheet lead, would, of course, account for the larger percentage of H in the evolved gases.

The measurement of the cell Zn | H_2SO_4 | PbS does not throw much light on the matter. Actual measurement gave 0.19 volt, the calculated voltage being 0.18 volt, taking the heat of the solution of H_2S into account. Great care is necessary in making this measurement or a wrong conclusion may be arrived at, because the resultant substance of the reaction is the very one we wish to avoid in the measurement. That is to say, if the cell

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is allowed to send a current, a film of spongy lead is produced over the complete surface of the PbS, and it then behaves to all intents and purposes like a mass of pure spongy lead. To take the first deflection before it has sent any current is also misleading, as there is apparently a film on the surface of some other lead compound which gives a reading of 0.68 volt. To get consistent results therefore, it is necessary to allow the cell to send a current to reduce this film and then amalgamate the film away with mercury. A surface of pure PbS is then produced which gives the above measurement.

It is a matter of gratification that the efficiency can be worked up to such a high yield considering the theoretical difficulties of the reaction and it is, therefore, all the more disappointing that the reaction cannot be brought to a completion; that is to say, that the last 5 per cent. of PbS cannot be reduced, as on reference to the curves it will be seen that it tails off in an aggravating way when about 5 per cent. of PbS still remains. This, of course, necessitates further treatment to obtain a pure product, which it is unnecessary to enter into here. A complete reduction of the sulphide would render the process an ideal one. The explanation offered is that a few particles of PbS become encased in lead sponge which then behaves to all intents and purposes like a piece of pure lead sponge, the reducing action of the current being unable to penetrate the casing. Another theory is that PbS prepared under different conditions, as I have repeatedly demonstrated, varies largely in its electrical conductivity and this 5 per cent. may be composed of what I might call non-conducting, or only partially conducting, sulphide. An attempt was made to prove this by dissolving the lead sponge in mercury and so leaving the PbS behind when it could be put under examination, but without success, however.

It has been previously mentioned that for experimental purposes it was necessary to keep the gases from the anode and cathode separate, and if it is not wandering too far away from the subject it might be interesting to refer briefly to the reasons for this. In the earlier experiments before this was done, some rather curious analyses of the gases were obtained, a few of which are given below:

H_2S.	H.	O.
9.6 per cent.	8.20 per cent.	8.4 per cent.
64.0 "	35.8 "	0.2 "

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It will be noticed that there is a curious absence of O, as, of course, it was expected that the volume of the gases would be in the ratio of two volumes of H and H_2S to one of O, and even should the H_2S act as a depolarizer at the anode to some extent, thus, $H_2S + O = H_2O + S$, this would not alter the relative volumes of the gases evolved and they should still remain in the proportion of 2 to 1. The absence of O, as shown in the above analyses, came therefore as rather a surprise. On investigation, however, it was found that under proper conditions H_2S could be oxidized to various oxy-sulphur compounds without passing through the stage $H_2S + O = H_2O + S$, as the liberation of free S would have been a necessary conclusion to the reaction. This depolarizing effect of the H_2S acts advantageously as, of course, it reduces the polarization of the cell. It is not, however, the object of this paper to go further into this, but it must be left over for another occasion.

Referring back to the singularity of the high efficiency of the reduction when compared with the difference in the thermo-chemical equations of the two reactions, I thought it would be interesting to see how far this applied to the sulphides of other metals. But the conditions are somewhat restricted, as it is necessary that (1) the sulphide should be a conductor; (2) that it must not be a sulphide precipitated from solution, as these are usually poor conductors due, no doubt, to their fine state of division; (3) that it should be capable of being prepared of reasonable purity; (4) that for the purpose of comparison its heat of formation should not be greatly higher or lower than PbS. Cu_2S seemed to come well within these confined limits as it is an excellent conductor; it is easily prepared in the mass by fusion; it can be prepared perfectly pure and its heat of formation is almost exactly the same as PbS, namely, 20,240 cal. The thermo-chemical equation then becomes:

$$\begin{aligned} Cu_2S = 2Cu + S &= -\ 20{,}240 \text{ cal.} \\ S + H_2 = H_2S &= +\ 4{,}510\ \text{“} \\ H_2O = H_2 + O &= -\ 68{,}360\ \text{“} \\ \hline & 84{,}090\ \text{“} \qquad (1) \end{aligned}$$

$$H_2SO_4\ aq = H_2 + O + H_2SO_4\ aq = 68{,}260 \text{ cal.} \qquad (2)$$

The Cu_2S was reduced under precisely similar conditions in every respect as the PbS, but vastly different results were obtained, as shown by Table V and curve Fig. 5:

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TABLE V.

Reduction of Cu_2S. Conditions exactly similar to those for PbS.
Current, 3.6 amps. Ore, 15 grams.

Time in minutes.	Gases.		Ore.	
	H, per cent. by volume.	H_2S, per cent. by volume.	Cu, molecular percentage.	Cu_2S, molecular percentage.
5	42.4	57.6	2.7	97.3
10	44.8	55.2	5.3	94.7
15	52.0	48.0	7.6	92.4
20	56.8	43.2	9.7	90.3
25	60.0	40.0	11.5	88.5
30	61.6	38 4	13.3	86.7
40	66.4	33.6	16.5	83.5
50	72.8	27.2	19.1	80.9
60	76.8	23.2	21.3	78.7
70	80.0	20.0	23.2	76.8
80	83.2	16.8	24.8	75.2
90	84.8	15.2	26.2	73.8
100	87.0	13.0	27.4	72.6
110	88.0	12.0	28.5	71.5
120	88.8	11.2	29.6	70.4
140	89.6	10.4	31.3	68.7
180	90.8	9.2	34.8	65.2

The percentage of H is always higher than the H_2S in proportion to the percentages of reacting substances (Cu_2S and Cu) present, which is just what would be expected from a study of the thermochemical equations. I am not prepared to admit, however, that the physical condition of the Cu_2S undergoing reduction is entirely irresponsible for this. After about the first hour it assumed a very bulky condition which would offer poor facilities for conducting the current and quite different from the spongy form which PbS assumes. But this would not account for the shape of the curve during, say, the first hour.

NiS also offers a suitable sulphide for reduction as it comes reasonably well within the above prescribed limits, its heat of formation being near that of Cu_2S. The gas curve, however, gives results differing largely from those previously considered, keeping at almost zero for some distance, rising to a maximum after about fifty minutes and then gradually falling. The percentage composition of Ni and N_2S undergoing reduction was not taken, as some of the reduced Ni, being in a very fine state of division, went into solution. The following results were obtained :.

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TABLE VI.

Reduction of NiS. Conditions exactly similar to those for PbS.
Current, 6 amps. Ore, 15 grams.

Time in minutes.	Gases.		Time in minutes.	Gases.	
	H, per cent.	H_2S, per cent.		H, per cent.	H_2S, per cent.
5	100	0.0	55	68.0	32.0
15	97.6	2.4	60	69.6	30.4
20	94.4	5.6	70	75.2	24.8
25	89.6	10.4	80	78.4	21.6
30	84.0	16.0	90	83.2	16.8
35	78.4	21.6	100	87.2	12.8
40	73.6	26.4	110	89.6	10.4
45	69.6	30.4	130	93.6	6.4
50	68.0	32.0	...	....	....

Ag_2S has a very low heat of formation and is in fact an ideal substance for efficient reduction.

$$Ag_2S = 2Ag + S = -\ 5{,}310 \text{ cal.}$$
$$S + H_2 = H_2S = +\ 4{,}510 \text{ "}$$
$$H_2O = H_2 + O = -\ 68{,}360 \text{ "}$$
$$-\ 69{,}160 \text{ "} \qquad (1)$$
$$H_2SO_4\ aq = H_2 + O + H_2SO_4\ aq = 68{,}360 \text{ cal.} \qquad (2)$$

It will be seen that the heats of formation in equations 1 and 2 are very nearly equal. The curve is very similar to those obtained for PbS, but shows a much sharper drop. It is necessary, however, to prepare the Ag_2S by precipitation, which, as a rule, gives a sulphide of high electrical resistance, but in the case of Ag_2S it seems to conduct fairly well. The following results were obtained:

TABLE VII.

Reduction of Ag_2S. Conditions exactly similar to those for PbS.
Current, 7 amps. Ore, 15 grams.

Time in minutes.	Gases.		Ore.	
	H, per cent.	H_2S, per cent.	Ag, mol. percentage.	Ag_2S, mol. percentage.
5	8.0	92.0	15.6	84.4
10	1.6	98.4	32.5	67.5
15	1.6	98.4	50.1	49.9
20	1.6	98.4	66.4	33.6
25	4.8	95.2	82.8	17.2
30	36.8	63.2	93.7	6.3
35	77.6	22.4	97.6	2.5
40	92.8	7.2	98.8	1.2
45	96.0	4.0	99.5	0.5
50	98.0	2.0	99.8	0.2
60	100.0	0.0	100.0	0.0

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Very few other sulphides are available for reduction, being either non-conductors, difficult of preparation in a suitable form, or of too high heat of formation. A sulphide which has a high heat of formation, as for instance FeS, is not reduced at all, nothing but H being evolved from the start, excepting in so far as it is acted on by the solution chemically.

A possible explanation of some of the above experiments is as follows. It has been above assumed that the number of calories necessary for the decomposition of H_2O is 68,360 or, expressed in volts, $\frac{68,360}{2 \times 23,040} = 1.48$ volts. It has been shown by Caspari and others that the voltage necessary to liberate H is not constant, but is dependent on the metal which constitutes the cathode. The excess which is necessary above 1.48 is what he calls the "over-voltage" (ueber spannung) and differs for different metals. There would have to be added therefore on to each of the above equations a certain "over-voltage" which might be sufficiently high to bring the volts necessary for the liberation of H *above* that for the liberation of H_2S, which would account for some of the unexpected results. This must not be relied on too completely however, as there is probably also an "over-voltage" for H_2S with different metals, which must be taken into account. What this is has not yet, as far as I am aware, been determined.

I have to thank Mr. P. G. Salom, president of the Electrical Lead Reduction Co., for permission to publish these researches.

DISCUSSION.

MR. C. J. REED: Mr. President, it seems to me that this paper is an exceedingly instructive one. It is particularly so to me, because, to my mind, it proves very conclusively what we should expect theoretically. It seems to me that these results instead of being difficult of explanation are exactly what we should expect. One sentence in Mr. Weightman's paper explains the whole thing, although he did not apparently seem to think so. He states that, where we have a mixture of cathodes, the current divides itself between the two in a proportion depending upon the accessibility of these two cathodes. It seems to me that that statement explains all these results very clearly. If we have a

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cathode consisting entirely of lead, we shall get nothing but hydrogen. If we have a cathode consisting entirely of lead sulphide, we shall get nothing but hydrogen sulphide. It seems to me this is a necessary conclusion. If we have only lead sulphide as a cathode and sulphuric acid as an electrolyte, no current can pass to the cathode without reducing lead sulphide, whatever may be the electromotive force required, and whatever may be the chemical energy necessary to produce that decomposition. As soon as current has passed into that lead sulphide, it reduces some of the lead on the surface. This gives a mixture of two cathodes, lead and lead sulphide. As the action proceeds the amount of the lead cathode increases and the accessibility of the lead sulphide cathode diminishes; not only by the quantity of its surface diminishing, but also by its higher resistance, which, other things being equal, would render it less accessible to current of a given electromotive force. It seems to me that those curves which Mr. Weightman has given here show this very beautifully. At the start he has no lead sulphide cathode; that is, he has a lead plate with some lead sulphide sprinkled over it in lumps. Lead sulphide is a comparatively poor conductor, and these lumps touch only at a few isolated points. Practically the only cathode is the lead plate, and, as I understand, he gets nothing but hydrogen at the start. But at those points of contact lead sulphide is very soon reduced to metallic lead, and then we have a good contact with the lead sulphide; consequently a much larger surface of the lead sulphide becomes available as a cathode surface; and that is the reason why the proportion of hydrogen sulphide rapidly increases after the first few seconds. When these pieces of lead sulphide have once made a good contact with the lead, they constitute by far the greater part of the available cathode, having perhaps a hundred, or maybe ten thousand times the surface of the lead plate. That accounts then for the percentage of hydrogen sulphide rapidly increasing up to a certain maximum and for the hydrogen sulphide remaining the principal product, until this larger surface of lead sulphide has been converted into metallic lead. As the cathode changes from lead sulphide to metallic lead, which will be a gradual process, the proportion of hydrogen sulphide will diminish gradually and that of hydrogen will increase.

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Finally some of the lead sulphide, as has been explained by Mr. Weightman, will remain practically inaccessible as an electrode, for its exterior surface becomes so completely covered with spongy lead that very little current can pass to the lead sulphide as a cathode. Consequently it is really out of the circuit. It seems to me this explanation applies to all of these curves, if we take into account the difference in the conductivity of the different sulphides mentioned.

In regard to the formation of hydrogen towards the end of the operation, and the high voltage required, Mr. Weightman should have taken into account something besides the formation heat of water.

The current which passes through sulphuric acid to a lead cathode from a lead peroxide anode is not simply decomposing water. It has a counter-electromotive force to overcome before it can pass through the system and, therefore, before there can be any decomposition of water or anything else. We have here a charged lead accumulator, which is being continually overcharged, a lead cathode, and a lead peroxide anode in sulphuric acid. It is evident that, in order to continue to pass a charging current through such an electrochemical system, the charging electromotive force must exceed the counter-electromotive force of this system, which varies in different conditions of charge from 1.73 to 2.44 volts, as I have previously shown in a paper on gas polarization in lead accumulators[1]. When fully charged the chemical electromotive force of this system is 2.44 volts and is no more dependent upon the formation heat of water than it is on the formation heat of PbO_2, SO_3, or any other component of the system. It is evident that no H_2O can be decomposed or H liberated with an electromotive force less than the 2.44 volts required to overcome the chemical electromotive force or electrogenic power of the system, as no current could pass through the cell with less electromotive force, and *current* is required to decompose water, not simply electromotive force.

The so-called "overpressure" of Caspari is not overpressure at all, but only the theoretical pressure required to overcome a counter-pressure of the electrochemical system. The term "overpressure" is based upon a false supposition that the

[1] "Gas Polarization in Lead Accumulators", Jour. Phys. Chem., January, 1901.

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normal pressure for the passage of current through all electrochemical systems containing water, is equal to the formation-pressure of water and that any additional pressure is overpressure, a supposition for which there is not the slightest foundation in theory or in fact. We might, with as much propriety, call the low electromotive force of the copper refining vat "under-pressure," because it is less than the decomposition-pressure of water. In both cases, and in all cases, the normal or proper pressure of an electrochemical system is determined by the chemical changes and the thermoelectric constants *opposing the current* and not by the decomposition pressure of water or of any arbitrarily chosen constituent of the system. The pressure in any case is represented by the well-known formula, $E = 0.000043\,C + T\frac{dE}{dT}$, in which C is the energy of the chemical change *tending to produce an opposite current.*

The pressure required for the passage of current in this system is, therefore, 2.44 volts, instead of 1.47 volts, because this is the counter-pressure of the opposing electrochemical system which has been generated by the passage of the current and which tends to produce a current in the opposite direction.

But we have present also and equally accessible to the current in this case another electrochemical system, consisting of sulphuric acid as electrolyte, PbO_2 as anode and PbS as cathode. The energy of the electrochemical system opposed to the current in this case is the same as in the other case, because the products of the current opposing it are the same, *viz.*, metallic lead and either lead peroxide or persulphuric acid, and the electromotive force of this system is 2.44 volts. Whether H_2S or H is liberated, depends only on whether the cathode is Pb or PbS, and not upon the formation heats of H_2O and PbS, since the electromotive force required to form the products of the reaction (Pb and PbO_2 or H_2SO_4) and, therefore, required for the passage of any current, is much greater than that required for the decomposition of either H_2O or PbS. The formation of H or H_2S depends only upon whether the current is obliged to make its exit from the electrolyte through PbS or Pb, that is, upon the relative accessibility of these two substances.

Therefore, as long as the PbS is in great excess and has good

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electrical contact, it will act as cathode and form H_2S, but as it becomes less and less accessible to the current, a greater and greater proportion of H will be liberated.

The conversion of a large proportion of the dissolved H_2S directly into H_2SO_4 at the anode would account for the small percentage of oxygen liberated.

DR. N. S. KEITH: The consideration of the secondary reactions taking place in this lead reduction is very interesting. I will not attempt to discuss it now, but it seems to me that we overlook the very simple fact that in order to effect this reduction we have to furnish a material which will combine with one or the other of the constituents of the cathode, lead and sulphur to form a new compound. We find *that* in the presentation of hydrogen, which, under the energy which is supplied to the circuit, unites with the sulphur which is thus freed from the lead, leaving, of course, metallic lead with the formation of sulphide of hydrogen. That is the prime, first, electrical reaction which takes place when the conductivity is so raised, and the conditions are such that enough of the surface of the lead sulphide is presented to the hydrogen which is set free. Then we can say that this action is, primarily, a decomposition of water, setting free oxygen at the anode at which it forms various secondary compounds; and the setting-free of hydrogen at the cathode at which, in its so-called nascent condition, it unites more readily with the sulphur than it could possibly with the lead, producing there the gaseous product, sulphide of hydrogen, which is set free. It seems to me the secondary reactions are certainly more complicated and are well considered in the paper.

MR. CARL HERING: The interesting results of Mr. Weightman bring up a point which seems to be very important in many electrolytic decompositions. It might facilitate matters to know what the theoretical voltages are, first, when hydrogen alone is generated and then when hydrogen sulphide is generated, also what the actual voltage was in the experiments. This so-called overvoltage may often explain things that may otherwise seem obscure. It would be interesting in this connection to know the origin of this overvoltage. It is not chemical; it is not due to resistance; it is not reversible. It has been suggested that it

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might be a thermoelectric counter-electromotive force, but it ought then to be reversible, which it is not.

MR. E. W. SMITH: I would like to suggest that the "overvoltage" alluded to by the last speaker is not the indefinite and uncertain quantity assumed, but is explained, and is pretty accurately expressed, by the Helmholtz equation for the energy changes in an electrolytic cell. Where A is the total energy change on which depends the voltage of the cell, U the chemical change, and T the absolute temperature, $A = U + T \frac{dA}{dt}$. The right-hand member of this equation represents the so-called "overvoltage," and I think accounts sufficiently for its existence.

MR. HUGH RODMAN: I was very much interested in Mr. Weightman's paper on sulphide reduction. It seems to me there must be a great variation here from the reaction we get in reducing the oxides or the sulphates or the chlorides of lead, whether in particles or in fused mass, particularly in the sulphate solution. With the film (which forms over these masses, starting from the cathode conductor) the reduction takes place much more rapidly. That film serves as a conductor and the current works through it to the mass of unreduced salt or oxide underneath. I do not see why it should not work so with the sulphide; that is, why it should not work through the film of lead sponge to the mass of sulphide underneath.

DR. F. HABER: Mr. President, I did not understand how Mr. Reed will overcome the difficulty that hydrogen will not develop on the cathode without overvoltage. I believe overvoltage creates a serious obstruction to the formation of hydrogen gas. I believe this obstruction will always exist unless some right intermediary step is taken; and I may instance mercury and the formation of a solution, or it may be an alloy, with the hydrogen. You will observe that the overvoltage is zero with platinum; and yet it is able to form an alloy with hydrogen. I believe no theory can give an explanation of the fact that we listened to to-day without considering this phenomenon of the formation of the solution, or of absorption or alloying between hydrogen and the metal such as I have spoken of.

PROF. R. S. HUTTON: Mr. President, we are all very much

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interested in the views of Dr. Haber. Whatever theory we may hold as individuals on the "overvoltage" subject, we are bound to take into consideration that it is with such metals as mercury and Pb that reductions have been accomplished, which were quite impossible with the same solutions and other metals as cathodes. We have a large number of reactions which have been thus carried out which could not have been carried out at all with other cathodes. In consequence, the reduction of lead sulphide would be expected to be very different from that of other sulphides. It would be interesting to know how the voltage is distributed between the electrodes in this electrolysis. It would also be interesting to know what takes place when the voltage is still higher than the value which Mr. Weightman seems to use generally.

It was not clear to me about the passing of the curve towards zero, which it never reaches. Towards the end about 95 per cent. of the gas evolved is hydrogen, and I suppose the balance is hydrogen sulphide. I do not quite follow how the two preserve that relationship without the remaining lead sulphide being gradually decomposed and all becoming metallic.

MR. E. A. SPERRY: I would like to ask about the velocity with which reduction takes place from sulphates after a film of lead sponge has overlaid the cathode.

MR. H. S. BLACKMORE: I would like to call attention to one fact which seems to me to bear on the relation between the reduction of oxide of lead and sulphide of lead by electrolytic hydrogen. When we reduce oxide of lead by hydrogen gas we produce a liquid which in the presence of the acids becomes a conductor and allows the current to reach other parts of the material, whereas in the case of the reduction of the sulphide of lead we produce a gas, hydrogen sulphide, which really isolates the body, and it seems to me that would explain the difference in the resistance.

MR. A. F. WEIGHTMAN: There were several points raised by Mr. Reed of considerable interest. I will try to answer him and Dr. Haber together. I do not think Mr. Reed is right when he ascribes this overvoltage as due to a chemical reaction between the spongy lead and the sulphuric acid or, in other words, that it is due to the solution pressure of the metal. If this were so the overvoltages of various metals would arrange themselves in the same

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order as their solution pressures, which is not by any means the case. For instance, Pb and Zn are fairly close together as regards their overvoltages, although their solution pressures are widely apart. As Dr. Haber pointed out in case of mercury, it is one of the metals which gives the highest overvoltage, although its solution pressure is low. The overvoltages seem rather to arrange themselves in the order of the melting-points of the metals (with the exception of palladium), but this may be merely a coincidence.

The increase of hydrogen sulphide Mr. Reed accounts for by saying that the reduction takes place at the points of contact and so the resistance of the ore is lowered, which is undoubtedly perfectly correct. I think I pointed that out in my paper. As regards the formation of persulphates, which Mr. Reed mentioned, I do not think the oxidation of the hydrogen sulphide is due to persulphates, because the oxygen is so completely used up. I showed in one particular case there was only 0.2 per cent. of oxygen in the evolved gases; and it is stretching the point rather too far to assume that 99.8 per cent. of the oxygen was used up in the formation of persulphate. This appears all the more improbable when it is considered that no special precautions were taken to have the conditions, such as temperature, current density and strength of acid, favorable for the formation of persulphates. I think it is really the saturated solution of hydrogen sulphide traveling to the anode, and there undergoing oxidation; but it seems to me rather an unexpected thing that it does not result in the simple equation $H_2S + O = H_2O + S$, which is what one would naturally expect.

Mr. Hering asked what the theoretical voltage was when hydrogen was evolved, presumably with a lead cathode, and then at what theoretical voltage H_2S was evolved, presumably with a PbS cathode. In the first case it will be

$$\frac{68360}{2 \times 23040} = 1.48V + x_1.$$

In the second case it will be

$$\frac{84250}{2 \times 23040} = 1.83V + x_2,$$

where x_1 is the overvoltage for H with a Pb cathode, and x_2 is the overvoltage for H_2S with a PbS cathode.

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x_1 is given by Caspari as 0.64 volt, which would make voltage necessary for the decomposition of water with a lead cathode $1.48 + 0.64 = 2.12$ volts.

x_2, if it exists, has not yet been determined.

I have not yet obtained the actual voltage in these two cases.

In the case of the reduction of the chlorides mentioned by Mr. Rodman I think it is a very different case from the reduction of the sulphides, and the comparison scarcely holds. If you calculate the thermochemical equation you will find the voltage necessary, for the reduction of lead chloride comes very near to that for the evolution of hydrogen. In the case of reduction of the sulphide it comes considerably above that for the evolution of the hydrogen. This would explain why the $PbCl_2$ reduces so much more completely and uniformly than the PbS.

In reference to Prof. Hutton's inquiry, I have not yet determined what the single potential difference at the cathode is, but since both gases are always present throughout the whole course of the reduction it will be at least as high as that which requires the higher voltage, and this is probably why the voltage curve keeps so steady (after once the contact resistance of the ore has been overcome), namely, that it is only registering the higher voltage of the two reactions.

Professor Hutton asked if the voltage was raised how it would affect the result. If you raise the voltage you raise the current. I have shown in my paper, the effect of raising the current density on the reduction, and it is rather a curious thing that it has very little effect on the efficiency.

PROF. HUTTON: How about the gases formed by using higher densities than those shown on the curve?

MR. WEIGHTMAN: The quickest reduction shown on the curves was at about a one-hour rate, and I do not think you can go much higher. Our usual time at the factory is about five days, so you will see that the one I show is at a particularly fast rate.

Mr. Hutton was not quite clear why the reduction curve did not come right back to zero. I am not quite clear myself, and can only refer him to the explanations offered in my paper. Of course when the amount of H_2S in the evolved gases gets very low it means that the current is doing very little work, and con-

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sequently the reduction of the ore proceeds proportionately slowly, and this is why the two curves run along almost parallel with the zero line.

I am not sure whether I understood Mr. Blackmore's remarks correctly, but he mentioned the reduction of oxide against that of sulphate. Of course, in the case of oxide, at least lead oxide, it will reduce far more readily than the sulphide, because if you calculate out the thermochemical equations of the two possible reactions which may take place, that is to say, the liberation of hydrogen or the reduction of the oxide, you will find the voltage necessary, for the reduction of the oxide comes very much below that for the liberation of the hydrogen, and consequently it would take place much more readily. But the reduction of sulphide requires a higher energy absorption than the liberation of hydrogen and, although it requires a higher energy absorption, it yet takes place more readily.

The question as to whether a gas or a liquid is liberated hardly comes into account. It merely comes down to this: that reaction which absorbs the least energy should take place the most readily, whether it forms a gas, liquid or solid.

MR. REED: Mr. President, I would like to correct one statement which, according to Mr. Weightman, I appear to have made. I did not intend to say that when a solution of hydrogen sulphide is at the anode, persulphuric acid or hydrogen peroxide or oxygen would be liberated. I do not believe that. The statement I made referred to the condition, such as you would have in starting, when there is only sulphuric acid at the anode. When the solution at the anode is saturated with hydrogen sulphide it becomes an entirely different case, and H_2S would, of course, be oxidized before any of the other products would be formed.

PRESIDENT RICHARDS: I have made some observations and calculations myself in regard to the voltage absorbed in this decomposition. Subtracting from the total drop of potential the voltage absorbed in conduction, according to Ohm's law (calculating from the conductivity of the electrolyte, the size of the plates, and the amperes passing), it left 1.87 volts as the voltage absorbed in decomposition. I do not know whether the figures allow of that accuracy, but this was, accidentally perhaps, within four one-hundredths of a volt of the theoretical voltage for the reduction, without allowing for any overvoltage effect.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 16, 1902, President Richards in the Chair.

DIFFERENCES OF POTENTIAL BETWEEN METALLIC CADMIUM AND SOLUTIONS OF CADMIUM IODIDE IN VARIOUS SOLVENTS.

By Louis Kahlenberg.

Determinations of differences of potential between metals and solutions in various solvents are relatively few in number. About two years ago I made, in my laboratory, at the University of Wisconsin, a series of measurements of differences of potential between metals and non-aqueous solutions of their salts, and the present investigation is a continuation of those earlier researches.[1]

In this work cadmium iodide was used as the solute because it is readily obtained in a pure anhydrous form, and is soluble in a goodly number of solvents, the resulting solutions often being fair electrolytes. Preliminary tests showed that cadmium iodide dissolves fairly readily in nitriles and amines, yielding solutions that conduct electricity. It was thought best to investigate the differences of potential between metallic cadmium and cadmium iodide dissolved in various nitriles and amines rather than to select a larger number of chemically very different solvents, as has been done in the previous investigations.

The cadmium iodide employed was pure and thoroughly anhydrous. The solvents used were of the C. P. variety of Schuchardt's make; they were carefully dehydrated and redistilled before using. It was sought to prepare solutions of the same strength in all cases,—namely, solutions containing one-tenth of a gram-equivalent per liter. This frequently succeeded, yet at times the salt was found to be so sparingly soluble that a solution of the strength just named could not be prepared; in such cases saturated solutions were employed, which were, of course, not strictly comparable with one another or with the tenth-normal solutions.

In making up the galvanic combinations for measurement of the potentials, the cadmium in form of a rod was dipped into the

[1] J. Phys. Chem., **3**, 379 (1899); also *Ibid.*, **4**, 709 (1900).

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cadmium iodide solution, and the latter was then connected with the so-called normal electrode of Ostwald, consisting of a normal solution of potassium chloride in contact with excess of mercurous chloride and metallic mercury. In all cases the cadmium was found to be the negative pole of the chain. The potentials were determined at 20° C. by means of the Poggendorff compensation method, a Lippmann's electrometer, sensitive to 0.001 volt, serving as zero instrument. Clark, Weston, and Helmholtz standard cells were used for comparison. It is unnecessary to enter into further details regarding the method of measurement as the latter has already been fully described.[1]

The results obtained are contained in the following table. In calculating the absolute difference of potential between cadmium and the cadmium iodide solutions, the potential of the normal electrode was assumed to be —0.56 volt, and the small electromotive force at the junction of the two liquids was disregarded. The third column gives the electromotive force of the total combination, and the fourth column the electromotive force of the *first half* of the chain.

No.	—	Voltaic chain.	+	Electromotive force. Volts.	Absolute electromotive force. Volts.
(1)	Cd	n/10 CdI_2 in water	N electrode	0.742	+0.182
(2)	Cd	n/10 CdI_2 in acetonitrile	N electrode	0.539	—0.021
(3)	Cd	n/10 CdI_2 in propionitrile	"	0.544	—0.016
(4)	Cd	n/10 CdI_2 in normal butyronitrile	N electrode	0.575	+0.015
(5)	Cd	n/10 CdI_2 in isobutyronitrile	N electrode	0.547	—0.013
(6)	Cd	n/10 CdI_2 in valeronitrile	N electrode	0.563	+0.003
(7)	Cd	n/10 CdI_2 in capronitrile	"	0.615	+0.055
(8)	Cd	n/10 CdI_2 in benzonitrile	"	0.611	+0.051
(9)	Cd	CdI_2 in *o*-toluonitrile	N electrode (saturated solution)	0.538	—0.022
(10)	Cd	CdI_2 in benzyl cyanide	N electrode (saturated solution)	0.564	+0.004
(11)	Cd	CdI_2 in mandelic nitrile	N electrode (saturated solution)	0.691	+0.131
(12)	Cd	CdI_2 in lactic acid nitrile	N electrode (saturated solution)	0.511	—0.049
(13)	Cd	CdI_2 in oxybutyronitrile	N electrode (saturated solution)	0.788	+0.228
(14)	Cd	n/10 CdI_2 in normal propyl amine	N electrode	1.039	+0.479
(15)	Cd	n/10 CdI_2 in isobutyl amine	N electrode	0.913	+0.353
(16)	Cd	CdI_2 in pyridine	N electrode (saturated solution)	0.718	+0.158

[1] J. Phys. Chem., **3**, 382 (1899).

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An inspection of the table shows that the highest differences of potential occur in the case of the solutions of the amines (Nos. 14 and 15). In normal propyl amine cadmium iodide dissolves with violent action and evolution of much heat; in isobutyl amine the reaction is less violent. All of the non-aqueous solutions above listed are poorer conductors of electricity than aqueous solutions of comparable strength, the solutions in amines being particularly poor electrolytes. The solutions in the simple nitriles (Nos. 2 to 20) yielded results that are of the same general order of magnitude, though the potentials are by no means identical. Considering solutions of comparable strength, the electromotive force seems to increase somewhat as the solvent advances higher in the homologous series. In the case of mandelic nitrile and oxybutyronitrile (Nos. 11 and 13) the voltages are exceptionally high, and one might be tempted to ascribe this to the oxygen content of these compounds, were it not for the fact that lactic acid nitrile (No. 12) yields a relatively low potential.

The difference of potential between a metal and a solution is undoubtedly determined by the chemical affinity existing between the metal and the solution. The results here presented serve to emphasize further a fact that appeared in the course of the previous investigations above mentioned, namely, that differences of potential between a metal and solutions of the same strength in solvents that are chemically analogous are of the same general order of magnitude, though they are by no means identical.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September, 16, 1902, President Richards in the Chair.

DEVELOPMENTS IN THE ELECTROMETALLURGY OF IRON AND STEEL.

BY MARCUS RUTHENBURG.

Many iron ores occur throughout the world, in the various iron-producing countries, which are too low in tenure to permit smelting. If these ores be magnetic, or rather, if the iron in the ores occurs as magnetite, that is, Fe_3O_4, it permits of a concentration that would not be possible if it occurred as either of the other two oxides. Concentration is essentially the separation of the valuable from the valueless portion, therefore there must be some difference between the portions of ores, either in the shape, hardness, gravity, or, in the case of magnetite, of the magnetic permeability, to permit of the separation of the particles so differentiated. In ores, in which the iron is carried as magnetite, it becomes one of the simplest and one of the most beautiful methods of separating the valuable from the valueless portions known to the art. Magnetites occur but seldom of such purity that they are entirely free from sulphur and phosphorus, and it depends very largely upon what portion of the ore these two metals are associated with, as to the fineness to which the ore must be ground, and its particular method of treatment in the magnetic machines. As a usual thing, the sulphur will be carried in separate and distinct grains or laminae of pyrite or pyrrhotite. The phosphorus may be carried disseminated throughout the mass as a phosphide of iron. It may be carried in apatite, or phosphate of lime. If the sulphur be carried as pyrite, elimination is simple, for the reason that pyrite is non-magnetic, and the magnets therefore do not lift it. If it occurs as pyrrhotite, its elimination is not so simple. The difference in magnetic permeability between magnetite and pyrrhotite being so small, the magnet strength requires very delicate adjustment. Except in the case of iron phosphide, elimination of phosphorus is quite easy, as it is carried by the non-magnetic gangue. The magnets leave it in the tailings.

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The essential feature is, to determine what fineness of mesh is required to release each individual particle from its neighbors, as it is quite evident that if not ground fine enough, the magnetic portion would drag a non-magnetic portion attached to it into the heads and therefore deteriorate the quality of the concentrates. It is found that when ores are ground finely and an attempt is made to magnetically concentrate them dry, there is a measure of adhesion between the particles of magnetic and non-magnetic portions that will not permit of cleanly work; this may be very prettily obviated by handling the ground ore in water, in which case the water seems to lubricate the particles so that the magnetic portions come away cleanly.

Having arrived at the point where the ore has been ground and concentrated magnetically in water, and is reasonably free from sulphur, phosphorus and deleterious gangue, we have a clean, fine, blue-black powder, which may carry anywhere from 65 per cent. to 72 per cent. of magnetizable iron, pure magnetic oxide being 72.40. It now becomes a question as to how this iron ore may be handled in a furnace. If an attempt be made to charge it into a blast-furnace, owing to its pulverulent condition, it will filter on down through the bed of fuel, and reach the tuyeres in an unreduced and unmelted condition. If an attempt be made to charge it into an open hearth or a reverberatory furnace, owing to its pulverulent condition, it is an extremely poor conductor of heat, and an intense flame may be played upon it for any length of time with the sole result of melting a plastic, pasty covering, leaving the inner portions of the mass unaltered. Many attempts have been made to put these powdered ores into manageable form by briquetting, or making them into bricks. To do this, it is simply necessary to thoroughly mix or agglomerate the powdered ore with some viscous material which will act as a binder, to hold the particles together. Many substances have been used for this purpose, many of them being the subjects of patents. To enumerate them, milk of lime, clay, bituminous coal dust, sugar-house waste, molasses, flour, starch, dextrine, tar, rosin, rosin-soap, silicate of soda, linseed oil and linseed oil substitutes have been used. It has also been proposed, and has been the subject of patents both in this and foreign countries, to add the iron dust to the coking charge of a bee-hive oven. Any of these methods under certain conditions make a reasonably good brick. Possibly the best is

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that in which from 5 per cent. to 10 per cent. of clay is used and the brick being subsequently burnt in a kiln, at not too high a temperature, the elements of the clay flux the iron into a solid coherent cinder-like mass. These clay bricks stand the operation of the blast-furnace well, if they have been well burnt. However they are not porous, and a furnace may not work very fast on such a charge and make a clean cinder. The lime brick is one of the most inviting propositions of the lot, inasmuch as the lime is an addition to the value of the charge of the furnace, which the clay is not, but a lime brick disintegrates almost immediately in the furnace. The hydrocarbon binders have had many advocates, but while they make an elegant brick, they do not stand the action of the furnace, as the carbon binder burns out before reduction and melting can take place. In any event, given a 70 per cent. ore to start with, the addition of 10 per cent. of any binder, reduces the iron content of the resultant brick to 63 per cent. The experience of iron furnace men upon these bricks for a charge has almost invariably been that as much flue dust is produced when running on bricks, as when running on 40 per cent. of fine ore unbricked.

In strong contrast to the above more or less successfully operated methods of handling these fine ores or concentrates, is the method that I have had in use for upwards of a year. It consists in taking the concentrates cleaned up to the highest point of possible purity, and putting them through an electric furnace, the melting zone of which is a magnetic field. The ore being magnetic, the magnetic field grabs and holds the grains of magnetite, and the polar projections of this magnetic field being at the same time the electrodes of the smelting circuit, the magnetic bridge thus formed by the ore forms a high resistance in the smelting circuit. The heat of the smelting circuit, therefore, is engendered within this bridge of ore itself. The electrodes are water-cooled and play no part in the melting, other than to conduct the current to the ore. The moment that the ore melts it loses its magnetism, and gathering weight from new molten material being added to it, it falls out of the magnetic field, its place being taken by fresh portions of ore from above. The result of this operation is agglomerated, coherent masses, ranging in size from a bean to a walnut, that are hard, strong, tough and porous, differing in analysis in no way from the ore, prior to its

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agglomeration, except for the absence of moisture and the last traces of sulphur. The product is in an ideal condition for use in the blast-furnace.

If reducing material, such as powdered coke dust or charcoal dust, be added to the charge prior to its introduction to the electric furnace, a partial reduction takes place and the fritted mass of carbonaceous dust and iron ore, partially reduced, is dropped into a soaking pit. If allowed to remain in this soaking pit a proper length of time, cementation takes place through the action of the heat left in the ore, by the electric furnace, and the action of the carbon fritted into the mass, which results in producing reduced metal, which may be properly termed steel. Any slag-forming material remaining in the ore through imperfect cleansing or magnetic concentration, remains with the metal. These materials in any event are comparatively small in quantity and are just what is wanted to protect the bath of molten metal in the open-hearth from the scorifying effect of the furnace. This material from the soaking pits is ideal for melting in the open-hearth furnace. It thus becomes possible to produce first-class steel direct from the ore, through the intermediation of the electric furnace and the soaking pit, producing spongy iron or steel ready for immediate melting in the open-hearth, without the intervention of the blast-furnace in any part. The blast-furnace, while well recognized as an economical machine, is essentially a concentrator, eliminating the gangue of the ore, the limestone and the ash of the coke as a cinder or slag. It costs far more, in fuel consumption, to melt a ton of cinder than it does to melt an equal quantity of iron, and inasmuch as all statements of economy are comparative, and it costs far less to grind and magnetically concentrate for the removal of the gangue, in that respect the blast-furnace ceases to be an economical machine. It also has the disadvantage of driving whatever phosphorus there may be in the ore into the resultant pig iron. The removal of this element from the ore by magnetic concentration is a decided advantage over the blast-furnace. It may be as well also, to remember the fact that the limestone and fuel charge are never entirely free from sulphur and phosphorus which, in the action of the furnace, are driven into the resultant pig iron, the phosphorus entirely and the sulphur partially; in fact, the sulphur and phosphorus of the pig iron owe their presence not alone to the ore but to the vari-

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ous components of ore, flux and fuel. In this electrical reduction, limestone is practically absent, fuel in contact with the charge is lacking, and reducing material necessary for the elimination of the oxygen of the ore is small in quantity and may, therefore, be selected of exceptional purity, without regard to its enhanced cost. Anything that will burn may be used for fuel to generate the electric current, which is the source of heat to be utilized in the reducing and melting of the ore. Poor coal, high in sulphur, high in phosphorus, even lignites may be used for fuel, as not even their gases come in contact with the ore and therefore play no part in establishing the quality of the reduced metal. If water powers of magnitude be available, they are sources of energy convertible into heat units not to be ignored.

It will certainly not be amiss to speak of one class of ore which has attracted attention for many years, but no advantageous method has been put forward of handling it. I refer to ferruginous beach sands. These occur in many parts of the world, the most notable being those of the St. Lawrence River and the Pacific coast of the United States. They also occur of greater or less richness in the West India Islands and Australia. An almost universal accompaniment of the magnetite in these beaches is titanium. The titanium generally occurs in separate grains of ilmenite. While the ilmenite is magnetic, it is less magnetic than the magnetite, and by gauging the strength of the magnets they may be made to take the magnetite and leave the ilmenite. These beach sands may readily be concentrated up to 71 per cent. of magnetic iron, out of the possible 72.40. The sulphur and phosphorus are almost invariably low, and these sands make one of the most inviting fields for this kind of work. Titanium frequently occurs, not only in these beaches, but also in the massive ore whose disintegration has formed the beaches. In the grinding of these massive ores, fine grinding and magnetic concentration in water will practically reduce the titanium to a negligible point.

Theoretically it has been stated, by various authorities that it takes from 3,000 to 3,500 kilowatt hours, to melt a ton of iron ore electrically. In my experience, I have succeeded in performing this fritting operation, either with or without reducing agents, with an expenditure of something less than 500 kilowatt hours. Every ore, of course, is a distinct proposition in itself,

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but there are few ores that will not stand the cost of this method of treatment. When we consider the vast quantities of low-grade ores, which cannot be economically treated in the blast-furnace, the field becomes a wide one. Any ore that will stand the cost of grinding, concentration and the various parts of the process of briquetting, will stand the cost of this fritting much more readily. The cost of the binder, whatever it may be, mixing, pressing, drying and burning cannot be done without an expensive plant and quite a considerable expenditure in the operation, saying nothing of the reduced value of the ore bricks, due to the addition of the binder. It must also be remembered that in the case of the beach sands nature has already ground the ore, and as these iron sands usually occur in or near the water, their environment is ideal for wet magnetic concentration.

DISCUSSION.

DR. EDWARD HART: Mr. President, there are some points in this paper that I wish to discuss. One of them is this magnetic concentration. I have had the pleasure this summer of seeing what I believe to be the best form of electric concentration. It is not, strictly speaking, magnetic concentration. It is being carried out on a small experimental scale in Denver by W. G. Swart. Most of the patents, I think, are those of Prof. Lucien I. Blake, of the University of Kansas. They have found it advisable to charge the particles of ore, of quite small sizes, many of them, with an electrostatic charge. Some of these particles take the charge more rapidly than others and lose it more rapidly. By the use of this fact they have been able to separate particles which are not, strictly speaking, magnetic. In other words, they have used a new principle altogether, and so far as I can see, from this experimental plant, the quantity of energy used is quite small. Further, they say that it is possible to separate in this way particles which cannot be separated very easily by water concentration, because of their extreme fineness. Mr. Swart told me that particles, for instance, which were much smaller than sufficient to pass a hundred-mesh sieve, were easily separated in this way, but it is necessary that the particles should be perfectly dry.

I think the author of this paper takes entirely too sanguine a view of the possibilities of the electric furnace in iron smelting.

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I am just as much impressed with the value of electricity as a new tool for the chemist as any one can be, but we must not allow ourselves to forget the work that has been done in iron smelting, and that to-day the iron-smelting furnace is the most economical furnace in existence, absolutely. When we consider that most of the iron furnaces would either have to forward their ore to some source of water power like Niagara Falls, or would have to generate the electricity from coal on the spot, and that the best steam engine gives not more than 15 per cent. of the available energy, you can see that the problem of smelting iron with the electric furnace is a pretty serious one.

DR. N. S. KEITH: I understood from the paper that the use of electricity is only preliminary to the subsequent use of the blast-furnace to produce the merchantable article. Whether the cost of the energy necessary to bring about that condition will prohibit it, is quite an open question. An item regarding the separation of pyrrhotite from magnetic oxide of iron is not quite clear. Pyrrhotite, as the author recognizes, is magnetic, and any magnetic separation will insure the accumulation of pyrrhotite with magnetite. If we can stand the cost of a preliminary roasting, so as to oxidize the sulphur of the pyrrhotite, this will change the iron contents of the pyrrhotite to a magnetic oxide, or magnetite, and thus eliminate one deleterious element of the original ore. I have my doubts as to the economic possibility of so preparing the ore for subsequent treatment in the blast-furnace. I am a great believer, and have been for years, in the utility of electricity, or electrical methods of preparing and treating ores, but in some cases economy absolutely prohibits its use.

MR. JOHNSON: In regard to the making of steel by electrometallurgical means, I would say that the person who attempts it competes against a "steam-shovel" proposition. A very large part of the iron ores comes from the shores of Lake Superior, is mined by the steam shovel, is very high grade, and consequently the cost of mining, per pound of iron turned out, is very low. In the case of magnetite, I believe Mr. Ruthenberg intends to treat clean ores. In that case, the cost of mining, and the cost of crushing, is all multiplied by two or three and sometimes by four or five, according to the percentage of iron in the ores. Therefore, it seems to me that any electrometallurgical

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process of making steel can only be successful provided the article which is made is so much better that it compensates for its higher cost. For instance, if the steel is made very hard and free from blow-holes, and has no dissolved gases in it, it has a physical texture which might compensate for its higher cost. Ordinary steel, made very cheaply, is good enough for most purposes, and steel made electrometallurgically must be of the grade of crucible steel. Otherwise the process has no economical value.

DR. HART: I am able to give some figures on this subject which I got this summer at the Mahoning mine, one of the best on the Mesaba range. They have taken out, by the aid of 50 men, 3 steam-shovels, and 3 railway trains, 12,000 tons of ore in one day, and the average cost of taking this ore out is 23 cents a ton. This ore is quite fine, easily broken up, and I suppose much of it, by the time it reaches the furnace, is almost in the condition of fine dust. I wish I knew more about the handling of fine dust in furnaces, but I do know that in most cases they have succeeded entirely in getting rid of the dust nuisance. I was told by a furnace manager in Pittsburgh that the amount of dust they collected in the dust-catchers using these ores, with a furnace turning out approximately 700 tons of iron daily, was about 15 tons, quite a small proportion when you consider the character of the ore. The quality of this ore ranges over 60 per cent. I think the Mahoning mine runs 66 per cent. iron and 0.05 per cent. phosphorus. This makes electric smelting as a competitor of the blast-furnace an extremely difficult proposition, economically considered.

MR. REED: Mr. Edison has a very difficult problem in the nature of the material that he is trying to concentrate. He starts with ore which contains on an average about 20 per cent. of iron. The rest is rock, which has to be transported to his crushers and ground to about fifty mesh. Then the ore also has a very large amount of phosphorus, and that was one of the principal reasons for the fine grinding. Then he tried to remove more of the phosphorus, at one time, by treating it with acid. Then it had to be washed and dried and briquetted. In the numerous operations to which he subjected his ore, it had to travel on conveyers from the time it entered the crusher until it came out as briquettes, about one mile. It is easy to see that with

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all those processes the final briquette must be an expensive product. But it seems to me that this does not prove magnetic separation to be impracticable. There are a great many places where the conditions are entirely different. There are immense quantities of magnetic ore that can be operated at perhaps one-fifth of this cost. Notwithstanding the fact that the ores from Michigan can be mined and put on the cars at 23 cents a ton, there is, nevertheless, a demand for magnetic ore in this part of the country at between $4 and $5 a ton.

MR. HERING: I understood Mr. Hart to say that the blast-furnace was very economical. I cannot agree with him, since the gases which leave a blast-furnace contain an enormous amount of energy, so much so that it has been claimed that if the gases were turned into power and sold, the pig iron could be obtained for nothing; this statement was made by some European who had studied the question closely. In Europe these gases are now being used largely as a source of power.

MR. JOHNSON: I believe in most blast-furnaces they use the waste gases to heat the blast in a hot-blast stove, and consequently they put the air in at a very much higher temperature, with the waste heat; although it is not used as economically as in a gas engine, still it does go back to the furnace. That is the reason that the blast-furnaces are made so much higher now and run much more economically.

MR. KEITH: As a further contribution to the subject, I will point to Mr. Edison's efforts in New Jersey in the way of producing iron electromagnetically. There they have a vast amount of rock which contains 20 to 25 per cent. of magnetite. An effort has been made to separate that magnetite by pulverizing the ore and passing it before the poles of magnets in Mr. Edison's peculiar way and separating magnetite, briquetting it, and then smelting it in the blast-furnace. I understood quite authoritatively that there is, in the production of iron, the question of limits of cost of about 60 cents per ton; that if at any time 60 cents were added to the cost of iron ore produced from Lake Superior, Mr. Edison could make a great deal of money.

DR. HART: I believe that there is a demand for anything in the way of iron at the present time. I was at Youngstown, Ohio, this summer, and a gentleman there, the manager of the

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furnace, was skirmishing all over the country to get something to put into his furnace. I think that partly accounts for it. I wish we could hear from Mr. Salom on this subject. I think he knows a great deal more about it than I do.

MR. SALOM: Mr. President, I do not see much likelihood, in the immediate future, of the electric furnace superseding the blast-furnace as a method of manufacturing iron or steel, but the possibility of its doing so is not to be ignored, in view of the improvements and discoveries that are constantly being made in electrometallurgical operations.

Some idea of the possibilities of electrical reduction can be had from taking the amount of energy required for reducing the ore and comparing it with the cost of the amount of fuel required by the blast-furnace.

The electrical equivalent for iron is 1.04328 grams per ampere hour, or, equivalent to about 870,000 ampere hours per ton, which at one volt would be 1160 horse-power hours, and, at the prevailing rate, $2.90 per ton. This figure, of course, would have to be increased by the amount of energy necessarily required to keep the ore and metal in the fused state.

Theoretically, 24 pounds of carbon would produce 232 pounds of metallic iron, and consequently, 207 pounds would produce a ton, or, in the ratio of about one to ten, according to the formula $Fe_3O_4 + 2C = 3Fe + 2CO_2$.

As a matter of fact, in the best blast-furnace practice, it takes nearly a ton of coke to a ton of iron, and while all the fuel is not used strictly for reducing purposes, yet, at the same time, it is necessary to have it.

When you think, therefore, that we are using nearly ten times the amount of fuel theoretically required to reduce the iron, it would seem as if there was some possibility in the future of reducing electrically. There are, of course, always losses in electrical methods, owing to the increase in electromotive force, over and above what is theoretically required to produce the result. While, therefore, there is a possibility of using electrical methods, the art will have to be very much more highly developed, and the cost of electric energy from water-power lower than it is at present before anything practical is done.

Referring to the concentration of ores, I think in view of the

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large amounts of high-grade ores that are still in existence, that all attempts at concentration processes will be a failure until the high-grade ores become scarce. Nobody wants to operate 5 per cent. and 10 per cent. ores, when they can get 50 per cent. and 60 per cent. ores. Concentration must cost something, and it is at a disadvantage to the extent of that cost.

MR. REED: There is no question that there are concentrating plants in existence that are not failures. In the northern part of New York, for instance, they are making hundreds of tons a day (and have been for years) of concentrated magnetite, and they are undoubtedly making money out of it; for example, the Chateauggauy Ore and Iron Company and the Witherbee-Sherman Co.

MR. SALOM: Those are not low-grade ores.

MR. REED: No, that is true, but some of them have a large amount of phosphorus, and are below 50 per cent. It pays to bring them up to over sixty and get rid of the phosphorus.

MR. SALOM: Yes, and that is the object of the concentration, in the first place.

PRES. RICHARDS: The statement is made in the paper that five hundred kilowatt hours would be used to frit together one ton of ore. I have made a calculation as to the efficiency which that means, and approximately it would mean an efficiency of 83 per cent. of the utilization of the heating power of the electric current to produce this result; that is, to heat the ore up to the fritting-point. Therefore, that power figure must be considered as a minimum; it would require at least that much, and probably more. The cost of five hundred kilowatt hours at $20.00 a horse-power year, or 6 cents a day, roundly, would be $2.67 per ton of ore treated. Mr. Ruthenberg's proposition is to take the already concentrated magnetic sand, and then frit it together. This would be the cost of preparing it, so to speak, for reduction, and would be entirely extra cost above all the cost of crushing, concentrating, and otherwise preparing the ore. In view of this, I think that the extra cost of $2.67 per ton for power alone (a minimum figure), rather points to the present commercial impossibility of the fritting process, since satisfactory briquetting can be done for 65 to 90 cents per ton.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 16, 1902, President Richards in the Chair.

ON THE FUSION OF QUARTZ IN THE ELECTRIC FURNACE.[1]

By R. S. Hutton, of Manchester, England.

During the last few years a great deal of work has been done, on a small scale, on the fusion of quartz, chiefly so far with the object of preparing quartz fibers and small tubes for scientific purposes. Quartz, sand, and other forms of silica melt at a very high temperature, giving a transparent glass-like substance—"vitrified quartz." On account of the exceedingly small coefficient of expansion and high melting-point of this substance, it possesses many valuable properties far superior to those of the best forms of glass hitherto commercially prepared.

All the attempts previously made to fuse this substance seem to have been with the oxyhydrogen blowpipe, but the fusing-point of quartz is so high, being considerably higher than that of platinum, that it is only with great difficulty and only in one small zone of the oxyhydrogen flame that it can be melted at all, and to work large masses in this way would be an exceedingly difficult matter.

Several experimenters have noted the effect of heating quartz in the electric arc, but all seem to have been struck by the chemical changes which it undergoes, being reduced to silicon and carborundum, and giving a black crystalline mass of either or both of these substances as a product of the action.

Upon taking up work on this subject some time ago, I was struck by the great ease with which silica could be melted in the arc and soon found that, whereas in the ordinary electric furnace with its reducing atmosphere, silica *is* reduced as above mentioned, still if precautions are taken to ensure an oxidizing atmosphere around the quartz, this substance can be very easily fused by the electric arc without any complications arising from the reduction.

My experiments at first were carried out with a small open arc with a magnetically deflected flame; under these conditions it was

[1] See Manchester Lit. and Phil. Soc. Proc., January, 1902.

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very easy to see the effect of the reducing or oxidizing atmosphere, for when the quartz was brought right close up to the arc a black spot was immediately formed on the fused mass, but if this was removed some little distance away the rising air soon re-oxidized the reduced part, giving again a transparent mass; in this respect, the working of quartz in an arc "flame" very much resembles the working of lead glass in the ordinary blowpipe flame except, of course, for the immense differences in temperature.

This preliminary work, although it demonstrated the possibility of fusing quartz easily by means of the electric arc, did not seem to me promising as a suitable process for working on a large scale and also offered peculiar difficulties, in that I did not consider myself a sufficiently expert glass-blower to expect to obtain results at all comparable with the beautiful work of Shenstone, who has by means of the oxyhydrogen flame laboriously built up most exquisite pieces of apparatus of fused quartz; I wished rather to work out some method capable of being used on a much larger scale than his for making this substance, which, as I shall point out later, is a material which would at once find most valuable uses.

Consequently, as being much more manageable and convenient, my next experiments were carried out in a small laboratory electric furnace, using a direct current arc of about 50 volts electrode potential and 300–500 amperes.

In this electric furnace, which is essentially of the Moissan type, I first attempted to prepare quartz tubes possessing thick walls and a small bore as I considered that such tubes would be very useful as a starting-point for making other tubes, bulbs and all kinds of scientific apparatus and would be much more quickly and economically prepared than by the method of Shenstone, which consists in building up a small tube by the fusing together of small silica rods previously prepared in the oxyhydrogen flame.

The method appears perhaps rather prehistoric in comparison with the present methods of making glass tubes, as it consisted essentially in making a mould and casting the tube in this mould.

Fig. 1, showing a section of the furnace, will help to explain this, while Fig. 2 gives a general view of the experimental plant. I shall not stop to describe the latter now as it is intended to

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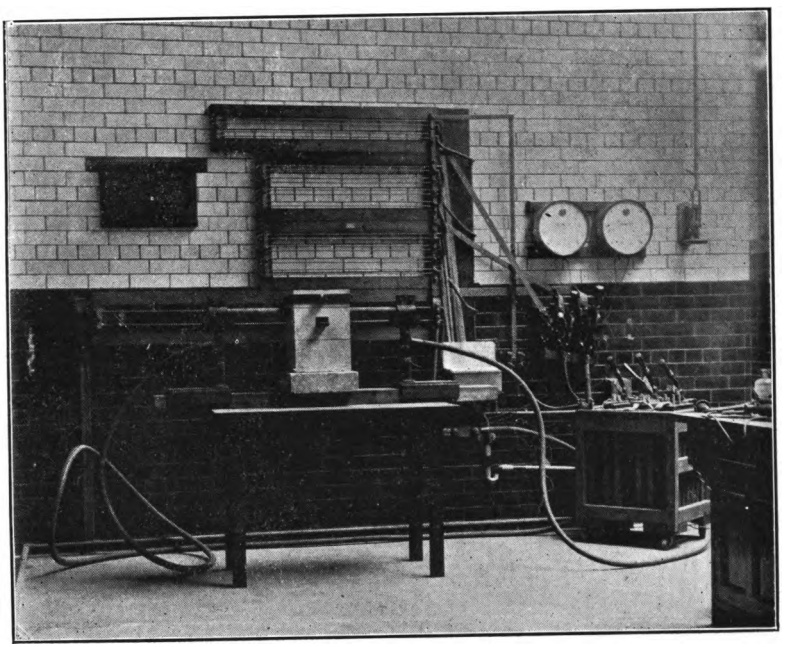

FIG. 1.

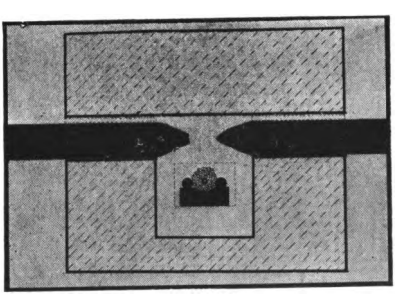

FIG. 2.

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publish shortly a description of this and other experimental electric furnace equipment of our laboratory.

As can be seen from the figure, and the model of the mould which I have brought with me, the mould consists of a graphite block about $24 \times 2^1/_2 \times 1$ inches, and is grooved out; as an axis, a small graphite rod, of about diameter of bore of tube required, is supported on end pieces. Around this axis the tube has to be built up; other rods placed in the grooves help to retain the material.

In this mould small pieces of prepared quartz crystal are placed. (The preparation, as described by Shenstone, consists in heating the quartz crystal in an ordinary crucible gas furnace to about 1000° C. and cooling rapidly by emptying the contents of the crucible into water; in this way a non-splintering material can be obtained which can then be heated as quickly as desired without any fear of its breaking up and flying about.)

It is not, however, by any means essential to use the prepared crystal in the electric furnace, provided a small amount of flying about of the crystals from one spot to another causes no detriment to the particular object desired.

The furnace consists, as shown in the figures, of blocks of limestone which enclose the arc; similar furnaces of graphite have been used and at any rate it is preferable to use a cover of graphite as the limestone breaking up is apt to contaminate the quartz.

The mould is fed gradually under the arc, the portion immediately underneath becoming very quickly fused, when the carbon is advanced little by little until the whole mass is fused along its entire length; in this way tubes of any desired dimensions could be made.

Several tubes were prepared in this way, some 10 to 20 inches in length, but with the small power at my disposal, I was never able to get results of any beauty, owing to the mass always containing a large number of small enclosed air bubbles which greatly impair its transparency.

No difficulty is experienced in removing the fused mass from the mould or in taking away the core. As there seems to be no tendency for the quartz to adhere to the carbon if both are pure, this is probably due to the formation of oxides of carbon which prevent the direct contact of the silica and carbon.

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The next experiments were made with small carbon crucibles, in which prepared quartz was placed, as upon these the heat could be more easily concentrated. Several lens-shaped disks were made in this way and only under these conditions have I been able to prepare a whole mass of actually molten quartz, for in the other experiments the material seems to become very plastic, to melt on the surface, and thus to flow into shape around the mould. In the crucible, however, the mass could often be seen running about in a very fluid condition, in fact in one experiment in which the side of the crucible had become burnt away the material was actually poured out of the carbon crucible. This seems to promise the possibility of casting the material when one has larger power available for melting it.

Pure sand was treated in a similar way but as yet without giving very satisfactory results. The fused mass seems to be much less transparent than when quartz crystal is used as a raw product, but this again may be due to the air bubbles which will certainly disappear so soon as the mass can be kept molten some time for them to rise. It may be well here to mention one or two precautions necessary for any one attempting work on these lines.

Firstly as to the quartz itself, this or any form of silica employed must be of quite exceptional purity, as even traces of metallic oxides (such as lime) which very readily combine with it would influence seriously the properties of the fused mass. On this account, also, the carbons used for the arc and for the supports should be of the greatest purity possible, and in this connection the Acheson graphite which I have used almost throughout is to be recommended.

While working on these lines, another method of forming tubes was tried, and although it also has not yet been carried to a very satisfactory conclusion, it may be well to mention it.

A carbon rod or carbon of any other shape required is brought to a white heat by passing an electric current through it, the carbon being surrounded by sand or finely divided quartz crystal. In this way, in almost a moment, the heating is sufficient to cause a powerful agglomeration of the particles of silica in the neighborhood of the heated carbon, and although by this process the material only becomes melted first on the inside near the carbon, still I believe such a method would be very useful for forming tube- or other shaped masses which could afterwards be melted

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in an electric furnace or by means of the oxyhydrogen flame. The whole process is so simple and so quick that large numbers of tube-shaped forms can be easily prepared and afterwards submitted to further treatment to fuse the walls into a transparent material. With regard to the applications of fused quartz, it seems almost unnecessary to mention the various uses to which a glass possessing the high melting-point and other valuable physical properties of fused quartz could be put. On account of the extremely small coefficient of expansion—the smallest of any known substance—assisted, perhaps, by the high thermal conductivity of this material, it is almost absolutely unbreakable by heat. Even very irregular masses can be suddenly heated to a white heat and cooled down in cold water or even liquid air without showing a tendency to crack. Then again the uniform composition of the substance renders it chemically very inert and resistent to attack by chemical reagents.

While the optical properties, especially the single refraction and transparency to ultraviolet light, have already caused many inquiries for this material, surely the demands for gauge glasses, lamp tubes, chemical apparatus, lenses and prisms should be enough to keep even the most active fused-quartz industry fully employed, could we but have it at our command.

At any rate, I sincerely trust that this possible application of electric furnaces may receive the serious attention which it seems at this moment to demand.

DISCUSSION.

DR. W. R. WHITNEY: Mr. President, I would like to ask Mr. Hutton if he has been able to overcome the difficulty of the opalescence, or the presence of many minute bubbles in the silica fusion. We have made small crucibles of fused silica and have found great difficulty in getting them perfectly transparent. They are apparently filled with minute air bubbles or some gas and we would be glad to know if he has overcome that difficulty.

DR. W. D. BANCROFT: While I have no official information on the subject, I understand that a number of successful experiments have been made on fusing quartz by means of the electric arc; that quartz has been fused in relatively large masses and obtained in a condition so that it has passed the viscous state and is entirely fluid.

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Mr. A. J. FITZGERALD: Mr. Shenstone, in his paper read before the Royal Institute, March 1, 1901 (*Nature*, May 16, 1901), refers to the difference in density that he finds in vitrified and natural quartz. Natural quartz has a density of 2.66, while quartz prepared according to his method has a density of 2.21. Mr. Shenstone prepares the vitrified substance by dropping fused quartz into water. I should like to inquire whether the quartz prepared by Mr. Hutton has its density altered in this way. Perhaps Mr. Hutton could give us some information of an interesting observation made by Mr. Lacelle. He found that by using tubes of quartz and heating therein a mixture of oxygen and nitrogen that nitric oxide was formed. In view of the work done at Niagara Falls by the Atmospheric Products Company, it would be interesting to know if any further experiments were made in that way.

DR. CHARLES A. DOREMUS: I had the pleasure in 1896 of seeing, at Sir William Crooke's laboratory in London, two Geissler tubes made from quartz. They were about three or four inches in length, with bulbs connected by a central tube. I would like to ask Mr. Hutton if those were of Mr. Shenstone's manufacture or that of Sir William Crooke's?

PROF. R. S. HUTTON: I am afraid many of the replies will not be quite definite enough, because I did not quite catch some of the details of the questions.

In reply to Mr. Whitney, I believe that the difficulties in the future as to these air bubbles will be very much lessened. When I first started I felt very despondent of ever getting anything approaching a transparent condition on account of the immense number of these small air bubbles. I found that the higher temperature and the more molten condition the material gets into, also the longer time it can be kept in the molten condition, the greater the improvement of the material in this respect.

Dr. Bancroft gives us some information as to quartz apparatus which has been prepared. I have, myself, seen some very beautiful things prepared by electrical methods in the fusion of quartz. The first were shown by Zeiss, of Jena, at the Paris Exposition. They had in a case fused quartz, simply labeled, "Fused Quartz Crystals." These, I understand, were prepared by an electrical method which consisted, roughly, of melting down by the electric

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current one single crystal of quartz, in a carbon crucible. I believe they found that the only method of preparing it at that time.

Mr. Fitzgerald tells us of some interesting work that he has noticed of Shenstone's. I hope I have laid sufficient stress on the admiration every one ought to feel with regard to this work of Shenstone's. He has really worked most carefully, and has obtained some beautiful results. I have seen several of the pieces of apparatus prepared by him and they are beautifully constructed, and I fancy it will be some little time before the electric furnace process is able to touch them at all. But the great point about the method of Shenstone is the immense time it takes. Shenstone recently exhibited before the Royal Institute in London, a prism of fused quartz which he had laboriously built up, gradually, piece by piece (the exact weight I do not know, perhaps a little over 100 grams), and which had taken a very considerable time to make. On account of the process by which he builds it up, the material is not uniform and requires a great amount of annealing to get it uniform at all. In France, also, they have done this by the oxy-hydrogen blowpipe method. The union of nitrogen and oxygen in the tube is an exceedingly interesting one. It has been known for a long time indeed that heat alone, if intense enough, will cause the uniting of nitrogen and oxygen.

DR. F. HABER: At the last meeting of our German Electrochemical Society, Mr. W. C. Heraeus, of Hanau, Germany, exhibited apparatus made from fused quartz. I mention his name as some of your members might, in view of the interesting paper of Mr. Hutton, wish to know where further information might be obtained.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 16, 1902, President Richards in the Chair.

VOLTAIC CELLS WITH FUSED ELECTROLYTES.

By Eugene A. Byrnes.

This paper is largely based on experiments which were made three years ago, with a view to determining the source of electrical energy in voltaic cells of the type in which the soluble electrode or anode is of carbon, the electrolyte a fused oxide or salt and the cathode of iron. This question was then the subject of considerable discussion between Ostwald, Anthony, Julius Thomsen, Liebenow and Strasser, Reed and Langley. Some held that the seat of electromotive force is at the surface of contact between the carbon anode and the fused electrolyte and that the current generated is primarily due to, and in greater or less measure proportional to, oxidation of the carbon at this surface. Others considered that the action is merely thermoelectric and due to differences in temperature at the junctions of the electrodes and electrolyte, occasioned by the externally applied heat.

The results of these experiments were not published, and thinking that they might be of interest to the Electrochemical Society, the earlier work has been repeated and a more general investigation of the subject of voltaic cells with fused electrolytes entered upon.

The electrolyte used throughout was primarily sodium hydroxide, contained in an iron or other vessel and maintained in fusion by a gas furnace. The electrodes were of carbon, especially graphite, and of various metals, generally in the form of thin strips. It became desirable to provide a diaphragm or porous cup by which the cell could be divided into two compartments to receive the two electrodes.

The preparation of a diaphragm which would fulfil the necessary conditions of porosity and non-conductivity and which would at the same time resist the fluxing or solvent action of fused basic oxides, was found to be a difficult problem. The ordinary porous clay cup is rapidly dissolved in fused sodium hydroxide.

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The first diaphragm tested consisted of a perforated iron cup having a lining of asbestos paper, held in place by iron wire gauze. In use, however, the asbestos was rapidly attacked. A porous cup was moulded from a composition of heavy magnesia and sodium silicate, shaped under considerable pressure in suitable metallic dies and fired at a high temperature while surrounded and filled with sand. This diaphragm was, however, converted into a pasty mass by subjecting it to the action of fused sodium hydroxide for a period of thirty minutes. Similar results followed the use of a porous cup moulded from a mixture of magnesia and coal-tar. A cup was cut out of a block of dense homogeneous quicklime, but it was unable to resist the fluxing and solvent action of fused sodium hydroxide. A diaphragm was now manufactured by taking two concentric cups of perforated sheet-iron, separated by a space of 1 cm., and filling this space with finely pulverized magnesia fire-brick which had been calcined in a steel furnace. This filling, however, became pasty in a short time. Finally an oxide was found which would resist the action of the fused caustic and it was used in granular form as a filling between the perforated iron cups, no binder which would enable a moulded cup to retain its shape being available.

The temperature of the electrolyte was at first determined by the use of mercury thermometers, reading to 360° C., and a resistance wire pyrometer. Afterwards, mercury thermometers reading to 550° C. were employed. The differences of potential at the terminals of the various cells were determined by Weston voltmeters, reading to 1/50 and 1/30 volt, a Weston millivoltmeter and a potentiometer having a resistance of 20,000 ohms, with a D'Arsonval galvanometer.

A normal electrode for the determination of single potential differences, of the type devised by Liebenow and Strasser, was also prepared. This consists of the well-known Ostwald normal electrode, in which mercury covered with mercurous chloride is in contact with a potassium chloride solution, but the tubular extension dipping into the cell in question terminates in a porous clay tube, the extension and tube being filled with the potassium chloride solution. The results of tests with this normal electrode were not satisfactory and it was not used.

In one set of experiments, both electrodes were introduced into an open vessel containing the molten sodium hydroxide; in the

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other set, the molten caustic was divided into separate portions by a porous cup and various oxidizing agents or depolarizers were supplied to the portion which contained the cathode.

The electromotive force of various couples in molten caustic held at a temperature of about 360° C. were found to be as follows:

1. Soft Swedish iron—high carbon steel = 0.00 volt.
2. Bright iron—iron coated with Fe_3O_4.

The electromotive force of this couple was found to be a function of the degree of oxidation of the negative strip. The voltage, starting at a low figure, could be progressively raised to a maximum of 0.32 by lifting the oxidized strip out of the caustic several times. Lifting out the bright iron strip simultaneously with the oxidized one made little or no difference in the reading. On removing and washing both strips, sandpapering the bright one and returning both, the reading was 0.30, again rising to 0.32 on lifting out either the oxidized strip or both. While the negative strip seemed to be coated with a continuous layer of the black oxide before its first introduction into the caustic, the experiment indicates that further oxidation or higher oxidation results from its contact with air while hot.

3. Copper—copper oxide = 0.20–0.25 volt.
4. Iron—graphite = 0.44.
5. Nickel—graphite = 0.20.
6. Copper—graphite. Low, but uncertain on account of rapid oxidation of copper.
7. Aluminum—graphite = 0.80. Falling quickly and regularly to about 0.10.
8. Magnesium—graphite = 1.25. Vigorous reaction and boiling.
9. Silicon—graphite = 0.86. Foamed so as to soon render reading uncertain.
10. Chromium—graphite = 0.03.
11. Gold—graphite = 0.12.
12. Silver—graphite = nearly 0.00.
13. Platinum—graphite = 0.19.
14. Titanium—graphite = 0.32.

In the experiments which follow, a porous cup was employed, the electrolyte in both compartments of the cell being fused caustic.

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15. Graphite in cup—graphite outside cup = 0.00.
16. Iron " " —iron " " = 0.00.
17. " " " —graphite " " = 0.44.

18. Various other metals, *e. g.*, nickel, chromium, silicon, magnesium, titanium, and silver, placed in the porous cup against the graphite cathode outside this cup, gave the same readings as when the cup was omitted.

19. The polarization value of sodium against graphite, due to the passage of two amperes between graphite electrodes inside and outside the porous cup and maintained at a potential difference of 4 volts for one minute, was about 2.30 volts.

20. Graphite cathode in cup—iron anode outside cup = —0.44.

21. With conditions as in preceding test, a few grams of potassium nitrate were introduced outside the porous cup. In one-half minute the voltage fell to 0.00 and began to reverse, rising in one minute to 0.35 and then to 0.385, where it held for ten minutes.

22. A few grams of manganese dioxide were then added outside the porous cup, quickly dissolving to give the green manganate. The reading then rose to 0.46, where it held. The cell was then short-circuited through an ammeter, giving a reading of several tenths, falling until the voltage was 0.30. On opening the circuit the voltage recovered in five minutes to 0.44 and in ten minutes to 0.46, the original value.

23. A strip of bright iron substituted for the iron cathode was almost immediately oxidized black and gave the same reading.

Other metals substituted for iron in the same depolarizer gave readings as follows :

24. Graphite, in cup—nickel, outside cup = 0.46. Nickel oxidized black when removed.
25. Graphite, in cup—gold, outside cup = 0.46.
26. " " " —graphite, outside cup = 0.46.
27. " " " —aluminum " " . Reversed to —0.70, falling quickly to —0.2.
28. Graphite, in cup—iron, outside cup = 0.46.
29. " " " —magnesium outside cup. Reversed to —1.00.

Various metals in the porous cup against graphite in the nitrate and manganate depolarizer outside gave values as follows :

30. Iron—graphite = 0.80, falling in one-half minute to 0.40 ;

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in one minute to 0.35 ; in five minutes to 0.32; in ten minutes to 0.30. The iron was oxidized black when removed.

31. Nickel—graphite = 0.42, falling in one-half minute to 0.16. Nickel oxidized when removed.

32. Aluminum—graphite = 1.30, falling in five minutes to 0.24.

33. Magnesium—graphite = 1.94, holding steadily at this figure for fifteen minutes, one-half inch being eaten off end of strip when removed.

In some experiments, anodes of amorphous carbon instead of graphite were employed, giving rather higher readings.

Various other oxidizing agents were tried as depolarizers, for example, lead dioxide, sodium dioxide, potassium bichromate, potassium chlorate, and nitric acid. Each of these agents, when dissolved in the caustic in one compartment, caused an iron electrode in that compartment to act as cathode toward a carbon electrode placed in fused caustic in the other compartment. Such different depolarizers, in general, gave different readings, but the tests made with them were not sufficient in number to establish any definite values.

Tests were made to determine the amount of carbon oxidized by the passage of a known current through the cell comprising a graphite anode in caustic and an iron cathode in a depolarizer. The current given by the cell itself being too small and inconstant to permit the loss of carbon by oxidation to be accurately determined, current from an outside source was passed through the cell from the graphite as anode, giving results as follows :

	Current.	Time.		Grams.
1.	9 amperes	183 minutes :	Original weight of graphite,	37.706
			Final " " "	32.128
			Loss in " " "	5.578
2.	1 ampere	600 minutes :	Original weight of graphite,	47.3476
			Final " " "	45.3185
			Loss in " " "	2.0291
3.	2 amperes	210 minutes :	Original weight of graphite,	45.3185
			Final " " "	43.9518
			Loss in " " "	1.3667

No. 1 corresponds to a loss for 96,540 coulombs of 5.445 grams.
No. 2 " " " " " 96,540 " " 5.440 "
No. 3 " " " " " 96,540 " " 5.242 "

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The reactions which occur within the cell employing a carbon anode, porous cup, and depolarizer, may be expressed by the following equation:

$$Q = (x\ CO + y\ CO_2) + (1/2\ Na_2O + 1/2\ H_2O) - NaOH - X.$$

The second and third terms in the second number of this equation cancel, that is, the sodium hydroxide is reformed by deoxidation of the depolarizer, and the total heat energy of chemical action apparent as electricity is that due to the formation of oxides of carbon minus that absorbed by reduction of the depolarizer. Since we are concerned in the above equation with the reaction of a gram-equivalent of each ion, the amount of carbon oxidized by the passage of 96,540 coulombs, which we may assume from the values given above to be 5.4 grams, must correspond to a gram-equivalent. A gram-equivalent of carbon as a dyad is 6 grams; of carbon as a tetrad, 3 grams. If x represents the fraction of a gram-equivalent of carbon oxidized to CO_2 by the passage of 96,540 coulombs, and y the corresponding fractional portion oxidized to CO, the following relations are obvious:

$$x + y = 1$$
$$3x + 6y = 5.4$$
$$x = 0.2$$
$$4 = 0.8$$
$$3x = 0.60 \text{ gram}$$
$$6y = 4.80 \text{ grams}$$

Thus 0.60 gram of carbon is oxidized to CO_2 and 4.80 grams to CO, if the proportions of CO and CO_2 produced in the voltaic cell are the same as those due to application of current from an external source.

This result is similar to that obtained by Coehn,[1] who found that carbon employed as an anode in dilute sulphuric acid was oxidized in part to CO and in part to CO_2, though the relative percentages found by him are different.

According to Julius Thomsen, the oxidation of a gram-atom of carbon to CO evolves 29,000 calories and its oxidation to CO_2 evolves 96,960 calories. If these values be applied to this cell, the oxidation of 4.8 grams of carbon to CO gives 11,600 calories and that of 0.60 gram of carbon to CO_2 gives 4,848 calories, a total of 16,448 calories. The voltage corresponding to the heat

[1] Ztschr. Elektrochem., 2, 541.

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evolved by such oxidation is 0.72, from which must be subtracted the voltage corresponding to the heat absorbed in removing a gram-equivalent of oxygen from the particular depolarizer employed.

The temperature curve of the same cell was plotted from readings taken at intervals of 5° from 290° C. to 540° C. This curve was found to be irregular and similar in form to those obtained by Liebenow and Strasser for a cell employing carbon and iron electrodes in a bath of fused sodium hydroxide.[1] The temperature coefficient of the cell is therefore not known with sufficient accuracy to enable the electromotive force of the cell to be calculated from the Helmholtz formula representing the total transformation of energy within a voltaic cell.

DISCUSSION.

MR. REED: Mr. President, I would like to ask Dr. Byrnes to define exactly what he means by a voltaic cell, and to state what evidence there is in any of these cases to show in which cases the cell is voltaic and in which cases it is thermoelectric. I think the conclusions we arrive at will depend very largely on the definition of a voltaic cell.

MR. BYRNES: By a voltaic cell I mean one in which electrical energy appears as a result of chemical action. Of course, in a general way, any battery gives electrical energy as a result of thermal action, but the term voltaic cell is commonly used to indicate a cell in which chemical energy, for example, that of oxidation at the anode or reduction at the cathode, is transformed into electrical energy.

MR. REED: In other words, the voitaic cell is one in which the electrical energy originates in chemical change or chemical energy, and not in heat?

MR. BYRNES: Yes.

MR. REED: Now, in the calculation of electromotive force, which has been given here, a large part of that electromotive force was due to the temperature coefficient, was it not?

MR. BYRNES: Yes.

[1] Ztschr. für Elektrochem., 3, 353.

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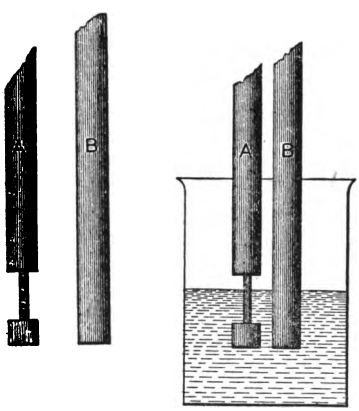
MR. REED: That part of the electrical energy must then be thermoelectric in origin, must it not?

MR. BYRNES: Yes.

MR. REED: It has been quite a number of years since I have looked into these figures, but some four or five years ago I spent a great deal of time in investigating the energy of the chemical reactions in these cells, and I found that with all the different changes from oxides of iron to metallic iron, and from one oxide to another, with the oxidation of the carbon electrodes, there was no case in which any energy could be evolved as electrical energy by the oxidation of the carbon and the simultaneous reduction of the iron to the metallic state, or from a higher to a lower oxide. I published those results in various publications and have not known of their having been controverted. But it is impossible to go through these figures off hand, and it may be that I was mistaken.

In connection with this subject, some years ago I experimented with electrodes of iron of different forms in fused caustic alkali. I found that by taking a round rod of iron and cutting it down to a small stem in one place, then taking another rod of the same size but not cut in that way, immersing them in a bath of fused alkali (see accompanying illustration) I found it very easy to get an electromotive force of 1.2 volts. This was described before the American Institute of Electrical Engineers in 1898. In that case, it seems to me, there is no possibility of any electrical energy being evolved by chemical action. In other words, that it could not be a galvanic cell in the sense in which Dr. Byrnes has defined it. The only source of any electrical energy must be heat. Consequently, it is a thermoelectric cell. It seems to me, therefore, that we cannot settle any of these questions as to whether the cell is thermoelectric or voltaic by merely measuring the electromotive force. In regard to the work of Liebenow and Strasser, I also gave (in the paper above referred to) considerable attention to



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their researches, and I found that by inverting the sign of their normal electrode, the electromotive force was in all their experiments proportional to the temperature.

DR. BYRNES: Mr. President, it is to be noted that various oxidizing agents give different values. Not only do they reverse the cell from one in which the iron acts as a soluble electrode or anode, to one in which the carbon acts as such electrode, but that they give different values according, apparently, to their efficiency as oxidizing agents. As to the thermal reaction which may express a portion of the electromotive force, I feel that it is only partial, and it may not even be the principal one. Whether the oxidation of the iron is intermediate between the oxidation of the sodium ion and the reduction of the depolarizer, I do not know. The depolarizer may act directly, as in the case of gold. It is a question whether the gold cathode would be to any extent oxidized.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 16, 1902, President Richards in the Chair.

A THERMO-ELECTRIC THEORY OF CONCENTRATION CELLS.

By Henry S. Carhart, LL.D.

The two classes of simple concentration cells of which I shall speak are as follows:

1. Two electrodes of the same metal immersed in a solution of a salt of this metal, the density of the solution being different at the two electrodes.

2. Two electrodes consisting of an amalgam of the same metal, both immersed in a solution of a salt of this metal, the concentration of the metal in the amalgam being different at the two electrodes.

My former paper before this Society was limited to the first of these two classes and dealt chiefly with the novel nickel-nickel sulphate concentration cell. Its most striking characteristic is the direction of the electromotive force in it, which is the opposite of all other well-known concentration cells of this type, for within the cell the current goes from the concentrated to the dilute solution.

It will be observed that the electromotive force of a concentration cell, calculated by the Nernst formula, given in my former paper, is proportional to the absolute temperature T of the cell. This fact suggests that the electromotive force of such a cell is of thermal origin; in other words, that the electromotive force of a simple concentration cell is the resultant of all the thermo-electromotive forces at the several contacts of dissimilar substances in the cell. From this point of view *concentration cells are devices for converting the heat of their surroundings into electrical energy.*

We shall arrive at the same conclusion if we consider the Helmholtz equation for the electromotive force of a galvanic cell,

$$E = \frac{H}{q} + T\frac{dE}{dT},$$

where H is the heat equivalent of the chemical reactions in the cell.

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If the temperature coefficient dE/dT is positive, then the energy given out by the cell electrically is greater than the chemical energy transformed, or the element tends to cool and to take heat from its surroundings. In my paper on "The Thermodynamics of the Voltaic Cell,"[1] I have shown that the heat given out or taken in when a voltaic cell is furnishing current without change of temperature is

$$T\left\{\left(\frac{dE}{dT}\right)_p - \left(\frac{dE}{dT}\right)_n\right\} dq,$$

the subscript p denoting the positive side of the cell and n the negative. One term is the thermo-electromotive force per degree C. for the positive side of the cell and the other for the negative side. The cell will neither give out heat nor absorb it when these two thermo-electromotive forces are equal to each other and of opposite sign; for then as much heat is generated on one side as is absorbed on the other. In the Daniell cell with concentrated solutions heat is generated at the negative electrode and absorbed at the positive in very nearly equal quantities, the thermo-electromotive force at both electrodes being directed from the liquid to the metal. But in the combination $Ni—NiSO_4—CuSO_4—Cu$, in which the copper is the cathode, heat is absorbed on both sides, and the cell has a very large positive temperature coefficient.

If the Helmholtz equation is generally applicable, it follows that when there are no chemical reactions and H is zero, the only source of electrical energy is the heat of the cell and its surroundings. The explanation of the electromotive force is then obviously thermal. From this point of view the nickel concentration cell does not constitute an exception, save that the thermo-electromotive force between the metal and a solution of one of its salts is directed from the former to the latter, while in the case of zinc, copper, silver, cadmium and others, its direction is from the solution to the metal. These facts have long been known. They are not sufficient to explain the electromotive force of a concentration cell without the aid of another law, which I have discovered; namely, the law of the increase of the thermo-electromotive force with the concentration of the solution, and of its decrease with the increase of concentration of the

[1] Phys. Rev., July, 1900.

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metallic ion in the amalgam. If the thermo-electromotive force between a metal and a solution of one of its salts were independent of the concentration, the thermo-electromotive forces on the two sides of the cell would balance each other, and there would remain only the relatively small electromotive force at the contact of the two solutions differing only in density. But the magnitude of the thermo-electromotive force is dependent upon the density of the salt solution, and the concentration of the metallic ion in the amalgam. Hence, with different concentrations the electromotive forces at the two electrodes do not balance, and the residual (neglecting any small potential difference between the two solutions) explains the electromotive force of the concentration cell.

Fig. 1 represents a $Zn—ZnSO_4—Zn$ concentration cell. The short arrows show the direction of the thermo-electromotive force at the two electrodes, the longer one of the two denoting the larger value on the side of the concentrated solution. The direction of the electromotive force of the cell will therefore be from the dilute to the concentrated solution through the cell.

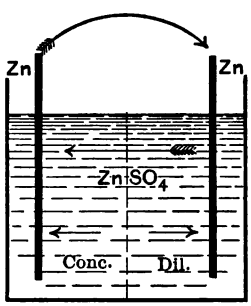

FIG. 1.

Fig. 2 represents a $Ni—NiSO_4—Ni$ cell. While the larger thermo-electromotive force is again on the concentrated side, it will be observed that the direction of these electromotive forces is the opposite of those with Zn and $ZnSO_4$. It therefore follows that the electromotive force of the nickel concentration cell is from the concentrated to the dilute solution within the cell.

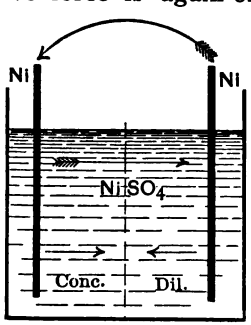

FIG. 2.

Fig. 4 shows the results of the determinations of the thermo-electromotive forces per degree C. for zinc and zinc sulphate with concentrations from $^1/_{100}$ gram-molecule to one gram-molecule to the liter. The ordinates are expressed in millivolts per degree C., the temperatures of the two sides being 0° and about 32°. The measurements were made by

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means of a cell similar to the one shown in Fig. 3. One limb of the cell was kept in a bath of ice-cold water, and the other in a bath of water at about 32°. A series of six such cells were placed in the same baths and were filled with the same solutions at different concentrations. The two electrodes were moved along from one cell to the next, measurements being made in each case twice,

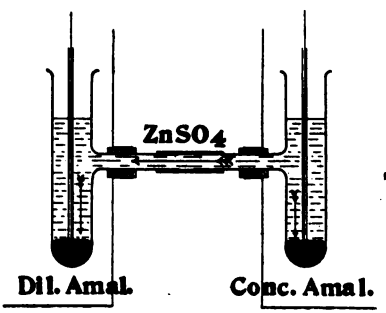

FIG. 3.

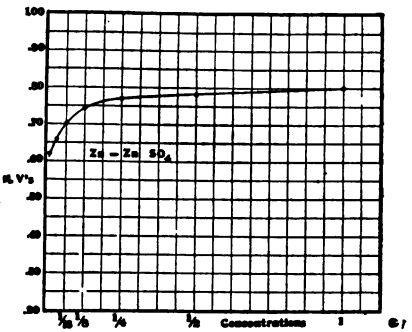

FIG. 4.

the electrodes having been exchanged between the two measurements for the purpose of eliminating any difference between them.

The electromotive force of a concentration cell set up with one gram-molecule and $^1/_{16}$ gram-molecule solutions of $ZnSO_4$ was found to be 0.02155 volt at 15.3°. If we consider only the electromotive forces at the two electrodes, the curve shows that the temperature coefficient should be the difference between 0.0008 and 0.0007, or 0.0001. Therefore the electromotive force at 15.3°, calculated from the expression $T\frac{dE}{dT}$, should be 288.3×0.0001, or 0.02883. The calculated value is somewhat larger than the measured value, indicating a probable thermo-electromotive force between the two solutions and directed from the concentrated to the dilute.

The curve of Fig. 5 expresses the relation between thermo-electromotive forces and concentrations for $Ni—NiSO_4$. It will be noticed that the scale for the millivolts is only one-tenth as large as in Fig. 4, while the scale for the concentrations is twice as large. The percentage increase of thermo-electromotive force with the concentration in the case of $Ni—NiSO_4$ is therefore enormously greater than for $Zn—ZnSO_4$. The electromotive force

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of the nickel concentration cell is also much greater than that of the zinc concentration cell. It is from twelve to fifteen times as large for the same concentrations and temperature.

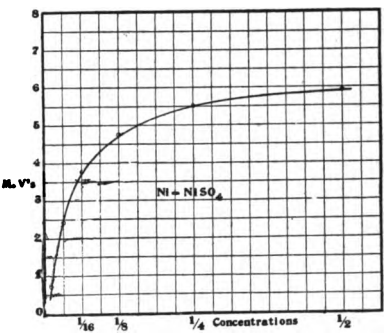

FIG. 5.

The second type of simple concentration cells is illustrated in Fig. 3. With a ratio in the concentration of the zinc ions in the amalgams of ten, and with a one-half gram-molecule solution of zinc sulphate, the electromotive force of this cell at 15° is 0.018. The current within the cell passes from the concentrated to the dilute amalgam, and the passage of a current reduces the difference in concentrations. The direction of the thermo-electromotive force is from the solution to the zinc amalgam, and is greater for the *dilute* amalgam than for the concentrated. Fig. 6 was plotted from the electromotive forces obtained by setting up the cell with the same amalgam in both limbs, keeping one limb at 0° and raising the other by steps from 0° to about 32°. Curve A is for the dilute amalgam, and B for the concentrated. These curves are nearly straight lines, and the corresponding thermo-electromotive forces are about one millivolt per degree for the dilute amalgam and a little less than 0.8 millivolt for the concentrated. In other words, the temperature coefficient of this cell should be about 0.00025 volt per degree. A direct measurement gave a value slightly over 0.0002.

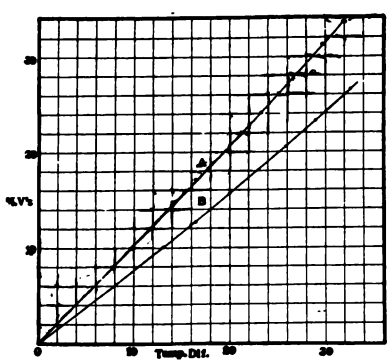

FIG. 6.

The electromotive force of this cell with amalgams of different concentrations is given by the formula

$$E = (T - t)\frac{dE}{dT}.$$

The constant t is about 190.

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The increase in the value of the thermo-electromotive force with the concentration of the salt solution has two important applications to the Daniell cell.

First. It is known that the electromotive force of the Daniell cell increases with the density of the copper sulphate solution, and decreases when the density of the zinc sulphate solution is increased. The supporters of the osmotic theory of the voltaic cell assert that osmotic pressure furnishes the only explanation of these facts. This proves not to be the case. The thermo-electromotive force on the zinc side of the Daniell cell gives rise to a negative temperature coefficient, and diminishes the electromotive force of the cell, while that on the copper side tends to produce a positive temperature coefficient and augments the electromotive force. Since both these thermo-electromotive forces increase with the density of the solutions, it is evident that the diminution of electromotive force of the cell when the density of the zinc sulphate increases is due to the augmentation of the opposing electromotive force of thermal origin. The curve which I obtained twenty years ago to express the relation between the electromotive force of the Daniell cell and the density of the zinc sulphate solution[1] bears a striking resemblance to Fig. 4 reversed. The diminution in the thermo-electromotive force when the density of the solution is increased multiplied by the absolute temperature gives the decrease in the electromotive force of the cell. A similar explanation applies to the rise of electromotive force when the copper sulphate is increased in density.

Second. Helmholtz says in his famous paper on "Chemische Vorgänge," 1882, that the temperature coefficient of the Daniell cell becomes zero with concentrated copper sulphate and with zinc sulphate of density about 1.04. Recent investigations show that the Daniell cell has a positive temperature coefficient when the density of the zinc sulphate is much reduced.

This variation of the temperature coefficient is also explained by the new fact which I have described. The temperature coefficient is equal to the difference between the thermo-electromotive forces on the two sides of the cell, the one on the zinc side being the greater except with very dilute solutions. Now when the thermo-electromotive force on the zinc side of the cell decreases with the density of the solution till it is just equal to that

[1] Am. J. Sci., November, 1884.

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between the copper and the concentrated copper sulphate, then the temperature coefficient becomes zero. A further weakening of the zinc sulphate solution causes the thermo-electromotive force on the zinc side to fall below that of the copper side of the cell, and then the temperature coefficient becomes positive.

DISCUSSION.

DR. W. D. BANCROFT: Mr. President, I was very much interested in this last account by Dr. Carhart, of the change of the temperature coefficient of the zinc sulphate when it was sufficiently dilute, because within the last year there has been a paper published by a Frenchman, Chaudier, in which he showed that if we dilute the zinc sulphate, the electromotive force rises, but if we dilute it enough the electromotive force passes through a maximum and then decreases again, which would seem to be entirely in accord with this fact, that had entirely escaped my notice, that the temperature coefficient of the zinc sulphate does change with increasing dilution. I would like to ask Professor Carhart if he knows whether experimentally these two changes, that is, of the temperature coefficient of the zinc sulphate, and this observed change in the electromotive force of the Daniell's cell under dilution, happened to coincide or not.

DR. F. HABER: I am geatly interested in the paper of Dr. Carhart. Concerning the relation between the thermoelectric power and the concentration of the solution, Dr. Carhart claims to have found a new theoretical law. It is very difficult for me to discuss this subject in a language foreign to me, but in my opinion the formula of Helmholtz, together with that of van't Hoff, covers the whole ground. According to Helmholtz the electromotive force is

$$E = \frac{Q}{n} + T\frac{dE}{dE};$$

van't Hoff on the other hand gives the equation

$$E = \frac{RT}{n} \text{ nat. log. } k + \frac{RT}{n} \text{ nat. log. } \frac{C \text{ orig.}}{C \text{ prod.}}$$

I give these formulas in their simplest form. C orig. means the concentration of the original substances, C prod. means the concentration of the substance produced. If there is no chemical

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change, Q and nat. log. k become zero and the relations then reduce to

$$\frac{dE}{dT} = \frac{R}{n} \text{ nat. log. } \frac{C \text{ orig.}}{C \text{ prod.}}.$$

For a further explanation I refer you to a paper published by me in the *Zeitschrift für Elektrochemie*, 1901, No. 75, p. 1043, Dec. 5, "Uber Electroden Potentiale."

MR. CARL HERING: Why would not a pin-hole through the diagram in Fig. 2 make it a perpetual motion? The electric current will, according to Professor Carhart, make the dilute solution more dilute and the concentrated solution more concentrated. Now, if the concentrations are the origin of the current, then by making a hole through the diaphragm the concentrations would neutralize mechanically and they would start afresh to produce this current, and that would be perpetual motion.

In saying this I do not wish to reflect on the observations of Professor Carhart, but simply on his conclusions that this was a concentration cell. I do not believe that it is, understanding by a concentration cell one in which the energy is due to the difference in concentrations, and is derived therefrom.

DR. LOUIS KAHLENBERG: About two years and a half ago I had one of my men make investigations on concentration cells of this nature. I should like to present a few of the results that were obtained. It was found that in the case of nickel chloride, where we used nickel electrodes and nickel chloride solutions as the electrolyte, that there, too, the nickel dipping in the dilute solution was the positive pole, as in the case of the nickel sulphate. In the case of cobalt, using cobalt electrodes and cobalt chloride solution as electrolyte, the same is true. The metal dipping in the dilute solution is the positive pole of the cell. The same is true when you use cobalt sulphate solution as the electrolyte and employ cobalt electrodes. The same is true when you use zinc electrodes and zinc sulphate as the electrolyte, provided you have a certain concentration of the solutions. This happens when you employ a normal solution of zinc sulphate and a one-thousandth normal solution of that salt. Dipping the electrodes in these zinc sulphate solutions the zinc in the dilute solution is the postive pole of the cell. But this reverses after some minutes. I do not know just how many minutes; perhaps five; and the

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current then flows as Professor Carhart has sketched it, so that you have a time factor in case of the zinc cell.

PROF. H. R. CARVETH: Mr. President, when we heard Professor Carhart's paper last year we decided to try the experiment with nickel sulphate dilute and nickel sulphate concentrated. We obtained results which conform very well with those mentioned; but we found that there was a time factor, and that with the nickel chloride the current actually reversed direction. There was a cetain amount of oxidation of the electrode which was quite apparent. However, when we repeated the experiment with the air absent, we did not find the reversal. We have not completed the experiments, and they are left in this rather unsatisfactory condition.

DR. GEORGE W. PATTERSON: Mr. President, it seems to me that the objection that is made to Professor Carhart's work, that a hole punched through the diaphragm would produce perpetual motion, neglects to take into account the source of the energy. Professor Carhart's observations are in too regular series, the points fall too closely on the curve, to admit of the supposition that a mistake is present. If you take the absence of mistakes for granted, in considering this cell we are to look around to see where we can get a source of energy. I can see no reason why we should not suppose that the electrode that cools takes heat from the surrounding medium, and the electrode which warms gives heat to the surrounding medium, but, of course, not so much as the other one takes, and there is produced a sort of thermodynamic engine. In the end, unless the heat of the surrounding medium is kept up from outside sources, undoubtedly it would decrease. This does not appear to me contrary to the second law of thermodynamics. We have an example right here in Niagara of that same thing. The water goes down over the falls and the heat of the atmosphere eventually gets the water back again. I cannot see that this cell involves anything more than the Niagara water-power does by way of a contradiction of the second law of thermodynamics.

MR. A. T. WEIGHTMAN: Various members have spoken from time to time of the solution of the nickel at one electrode and its deposition at the other, as if the deposition of nickel from a sul-

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phate solution were the easiest thing in the world. It is, however, a matter of common experience that this is a very difficult matter, at least by a separate current, and I see no reason why it should take place any more readily in a concentration cell.

Of course if there is no deposition of nickel at one electrode there cannot be a solution of nickel at the other, at least not as the sulphate. After hearing Professor Carhart's paper in Philadelphia I had the curiosity to try a few crude experiments on this point; and on short-circuiting the cell and allowing it to remain short-circuited I found I got no deposition of nickel at all in the dilute solution. Although the electrode in the concentrated solution lost a certain amount of weight, it did not lose the weight by going into solution as the sulphate, but a hydrate of nickel was deposited and presumably hydrogen was liberated at the other electrode although I did not detect it because the current was too small. If this is the case the cell must not be considered as a concentration cell with two nickel electrodes, but as a concentration cell with a nickel and a hydrogen electrode. I am aware that the heat of formation of NiOH is not sufficient to displace H from water, and there must therefore be some additional source of energy to bring about this reaction.

I would like to ask Professor Carhart whether he observed the deposition of nickel in the dilute solution; if so, how he reconciles this with the fact that the deposition of nickel from a sulphate solution is an almost impossible thing.

MR. C. J. REED: I do not understand how Mr. Weightman could have found that the anode lost weight by the deposition of nickel hydrate upon it. If it lost weight it certainly could not have been by the deposition of anything upon the electrode.

MR. WEIGHTMAN: There was not a deposition of hydrate on the electrode, but a precipitation in the solution.

DR. BANCROFT: I would like to call attention to one point which has only just occurred to me and which, therefore, I have not had time yet to think over and cannot vouch for. The calculation, of course, assumes that you have a reversible electrode. There seems to be no question but that in the case of nickel and nickel sulphate you do not have strictly a reversible electrode and that, therefore, the theory does not apply. That, however,

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is not sufficient. We have still to find some sort of an explanation why the current should go in the other direction, and it has just occurred to me that there may be an analogy here. If we consider the rate of the oxidation of sulphites by the oxygen of the air, we find that it is accelerated by the presence of manganese salts, nickel salts and various others, and that the acceleration increases with the concentration of the salt. Suppose we have here an oxidation of nickel by the oxygen of the atmosphere. That might, under these circumstances, easily take place more readily in the more concentrated solution than in the more dilute solution, and in that case the nickel in the concentrated solution would be more attacked, which would account qualitatively for the direction of the current. I do not care to vouch for this as an actual explanation, but it seems to me to have certain possibilities about it.

DR. KAHLENBERG: It seems to me this question can only be settled by inspecting very carefully the products that form at the electrodes, while the cell is in operation.

DR. W. R. WHITNEY: I would like to ask if Mr. Weightman can tell us whether he noted any diminution of the weight of his nickel electrode in the dilute solution. He said he observed it in his strong solution. It might serve as a proof of what Mr. Bancroft has suggested.

MR. WEIGHTMAN: I have not any data. I weighed the electrode and noticed a certain loss of weight—a few milligrams. The experiment was not made quantitatively as the current from the cell was not measured.

PRESIDENT RICHARDS: I should like to ask Professor Carhart whether there is any perceptible difference in temperature between the two electrodes to account for a thermoelectric source of the current. My idea of a thermoelectric battery is one in which there is a difference in temperature, which accounts for the electric current flowing from materials of different nature from one to the other or from the other to the first, perhaps, as the temperature rises. That has been my conception of a thermoelectric current, and I see no reason to call in thermoelectricity, if that is what is meant by thermoelectricity, to explain a cell which gives a voltage with all its parts at a uniform temperature.

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After listening to Professor Carhart's paper in Philadelphia, and listening to this now, I am still as firmly convinced as ever that chemical action is the source of the electromotive force.

MR. H. S. CARHART : Of all concentration cells ?

PRESIDENT RICHARDS : Yes; that chemical action is the source of electromotive force where the parts of the cell are at a uniform temperature and where we have the possibility of chemical action, such as the solution of the salt in a dilute or a concentrated solution, or the possibility, as has been pointed out by Mr. Weightman, of oxidation and the formation of other products,—of different products,—in the dilute or concentrated solutions ; or, as has been suggested by Prof. Bancroft, the possibility of different catalytic action of the dilute and concentrated solutions producing different chemical actions at the two electrodes.

DR. N. S. KEITH : I have found that in nickel solutions, those used for nickel-plating and experimental work, such as sulphates and chlorides of nickel, in endeavoring to effect commercial electroplating, there is a continuous action on the anodes, and if the cathodes of another metal be covered by nickel, there is an action upon those also, when there is no current flowing from any external source. The tendency is to the formation of hydrates and various subsalts of nickel. The same takes place with iron solutions where you use chlorides, sulphates, and other salts.

PRESIDENT RICHARDS : May I ask Dr. Keith whether the action will be different, or if he observed a different action, in dilute and concentrated solution ?

DR. KEITH : I made no experiments, but I should judge it would only depend upon concentration so far as the rate is concerned.

DR. CARHART : Mr. President, replying to Professor Bancroft's question in respect to the French observations, I remember reading some few months ago I think, the same ones he referred to, and the results given there are rather too erratic to be relied upon. They have not been confirmed. Now, I hope you will admit that I have a fair degree of experimental skill in these matters, but I confess to you, that so far I have not been able to measure the temperature coefficient of the Daniell cell with extremely dilute solutions. If any of you can do it with great

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reliability I should be glad to hear from you. I expect the oxidation effects come in, as they certainly do all the time, and make the thing irregular ; and greater changes than the changes due to temperature have been involved in the observations of this French gentleman. There is no question that the temperature coefficient does fall as the zinc sulphate becomes more dilute, but at what point it becomes zero I have not been able to determine. I have not given the thing up as hopeless, but I have not been able to solve the problem.

I think Professor Haber has misunderstood my statements represented by these curves. They do not represent the temperature coefficient of a concentration cell. They are the relation between thermoelectromotive forces and concentration, the concentration being the same throughout the cell. So it is a thermoelectromotive force depending on the fact that one side of the cell is heated and the other kept at zero when the solution is the same throughout, and not a temperature coefficient of the concentration cell itself.

In reply to Mr. Hering, the perpetual motion idea has not troubled me as yet, because I have made no affirmation whatever in reference to the concentrations, or the change of concentrations. I think you will all observe that. The current flowing through such a cell is so small that a change of concentration would be difficult to detect. I am glad to hear about the observation of Mr. Weightman in respect to that point.

I have used chlorides also, as Professor Kahlenberg has, using a pure chloride salt prepared in the Laboratory of Physical Chemistry for their special investigations, and I obtained qualitatively the same result as with the sulphate.

I have tried cobalt only once and I did not find this electromotive force in the reverse direction. Perhaps I should make further experiments on that point.

I found, also, a reversal, especially when the cell was first set up. If you measure immediately you may get a small electromotive force in one direction and after a little it goes in the other direction. I have been satisfied that the air has something to do with this. You will recall the experiment of Maxwell, with a tube filled with sulphate and zinc electrodes, in which the SO_4 comes down and the Zn goes up, the SO_4 being the heavier, so that the

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top is the cathode. Maxwell found, as probably you have if you have tried it, that the least bubble of air in the tube will make the thing so erratic that it is impossible to make the measurements. I have tried it, and as the little bubble goes up and touches the upper electrode, the balance is immediately destroyed and the galvanometer swings off the scale. It has been my intention to prepare a cell of this sort from which I could pump out all the free air possible, and see the effects, but I have not been able to do that as yet. I suspect there will be an effect produced.

I have not observed any deposition, because I have not allowed a current to flow any length of time, but have measured electromotive forces rather. Please observe this paper is not restricted to the nickel cell at all. It is applied to the zinc cell as well, and I have contemplated the subject purely from the point of thermoelectromotive forces. From that point of view all these fall in the same group.

I cannot agree with Professor Richards that there is no possibility of the origin of thermoelectromotive forces in cases like this unless we have differences of temperature, higher temperature on one side than the other. That is true where we have metals in series, as is well known. But here we have no thermoelectromotive force between metals, but between a metal and a solution. I should like to call attention to the famous Helmholtz equation which contains a term proportional to the absolute temperature. Also to a fact which I think is now admitted, that when that temperature coefficient is positive, as occurs in a few cases, that the energy output of the cell, electrically, is greater than the energy transformed chemically, and this excess comes from the fact that heat is converted into electrical energy. I have had occasion to make a large number of experiments on this point. As some of you may recall, in an article a couple of years ago in the *Physical Review* in the case of the Daniell cell, I stated that I obtained the difference in temperature due to the current flowing and corresponding exactly with theory, separating the two terms on the two sides; and I do not think there is any question that we have in that case, superadded to the energy of chemical action, energy coming from the addition of heat. If that is admitted, and I think it is, it does not trouble me that there is thermal energy and electrical energy in a concentration cell, while there is no chemical change taking place.

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I asked our president a question whether he affirmed that the energy of all concentration cells (waiving the point whether a nickel concentration cell is a real concentration cell) whether the energy coming from any concentration cell, is necessarily chemical. If it is we shall have to revise a good deal of physics. I supposed it was assumed that in the true concentration cell the source of the energy is not chemical.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 16, 1902, President Richards in the Chair.

AN ELECTROCHEMICAL PARADOX.

By Carl Hering.

If one who is conversant with the underlying laws of electrochemistry were asked if it were possible to decompose appreciable quantities of water with about a third of a volt, he would no doubt answer that it is not, as the oxygen and hydrogen which are formed could, by recombining, give off more energy than that which corresponds to this voltage, which would mean that in such a cyclic process more energy could be set free than was consumed, and that would be perpetual motion.

A description of an experiment made by Mr. C. J. Reed and the writer some years ago in which water was actually and visibly decomposed with only about a third of a volt may, therefore, be of interest; but in describing this curious experiment, the writer wishes it to be understood that he does not offer it as proof of the incorrectness of either the law of the conservation of energy, or of Faraday's law, which are the foundation stones of electrochemistry, but on the contrary he believes that an explanation in accordance with these laws must and will be found, and that if we cannot find it, it is our fault and not that of these laws.

The experiment is furthermore of interest as showing how dangerous it is to draw hasty conclusions concerning the framing of new general laws or the overthrowing of accepted ones from a single experiment. Suppose for instance that the result had not been paradoxical, it would have been natural to have accepted the facts without question, and perhaps the experimenter might have formulated a general law to account for them. It shows the importance of repeating an experiment in different forms and under different conditions, before definite general laws are deduced from it, or accepted laws overthrown by it. It also shows how easy it is to make an experiment to show that Faraday's law or the law of the conservation of energy fails, when the fault really is that these laws were not applied correctly.

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The experiment was as follows.—We supposed, as most others do, and as been demonstrated by other experimenters, that the voltage of decomposition of water increases with the atmospheric pressure. But to our great surprise the voltage sank gradually, steadily, and very decidedly as the pressure increased, until the apparatus exploded at a pressure of about 23 atmospheres, at which time the water was being decomposed at about 0.3 volt; that is, at about one-fifth the theoretical voltage as required by Thomson's law.

The details of the experiment are as follows.—Referring to the adjoining figure, the apparatus consists of an N-shaped glass tube sealed at both ends and containing water acidulated with sulphuric acid in one end and mercury in the lower bend; the end containing water had two platinum wires fused through the walls of the tube; behind the other end, which served as a manometer tube for measuring the pressures, was a scale. The gases which were set free by electrolysis generated a pressure in the tube, which pressure gradually increased as the current continued.

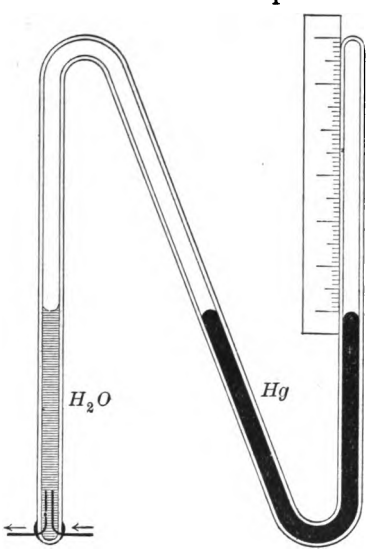

FIG. 1.

Our first intention was to generate a pressure by electrolysis, and then measure the lowest voltage at which a current would pass. But this gave no definite results, as the current seemed to increase gradually with an increase in voltage without any well-defined bend in the curve of results. We therefore passed a certain constant current of a small fraction of an ampere continuously, and took simultaneous readings of the difference of potential and of the mechanical pressure. This was continued until the tube burst. The whole apparatus was placed behind a strong shield to protect the eyes of the observers from the explosion, and the pressure readings were made through a small, thick plate-glass window in the shield. The explosion, however, was a mere

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puff owing to the small quantities of gas which were confined in the tube. As nearly as can be recalled, the tube was about an eighth of an inch inside diameter, and about 12 to 18 inches long. A fact which may be of importance was that the two platinum wire electrodes were, of necessity, quite close together, not too close, however, to prevent our seeing that both were gasing freely while the current passed.

The accompanying curve shows the results which were obtained. The measurements were not made with great precision as the test was not intended for more than a crude one, but the fall of potential and the rise of pressure were so great and decided, that the greatest possible errors would not change the general nature of the curve. About twenty readings were taken over the range shown by the curve.

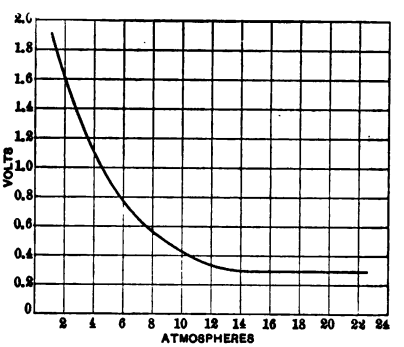

FIG. 2.

It will be seen that the voltage fell rapidly at first for a few atmospheres, then more gradually until it seemed to reach a minimum value of about 0.28 to 0.29 volt at about 15 or 16 atmospheres, which voltage seemed to remain practically the same for increasing pressures until the tube exploded at about 23 atmospheres. During all this time, to the very end, the gases could be seen coming from the electrode, so that there is not the slightest doubt that decomposition was taking place all the time; the fact that the pressure was being increased by these gases was sufficient evidence alone.

The constant current was led off as a shunt current from a potentiometer wire which enabled the voltage to be varied very gradually so as to keep the current through the apparatus constant. The voltage was measured at the terminals of the cell while this constant current was flowing.

The results become still more curious when allowance is made for the voltage lost in overcoming the resistances. Near the beginning, when the pressures were low, the voltage was about 0.4 to 0.3 volt higher than the theoretical voltage of the decomposition of water, namely, about 1.5; this, therefore, may be

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taken roughly as that lost by resistance. Now, assuming the resistance to have remained constant (which is probably only approximately correct), this loss of 0.4 to 0.3 volt should be deducted from all readings (as the current was kept constant) in order to show the true voltage of decomposition of the water, and it will then be seen that for pressures above about 15 atmospheres, the voltage of decomposition was very nearly zero, as about the whole of the voltage was lost in the resistance. This would explain why that part of the curve was flat. The measurements, however, were too crude and the uncertainty of the constancy of the internal resistance too great to conclude from this anything more than that the true voltage of decomposition at high pressures was still lower, and perhaps considerably lower, than the observed voltage 0.3.

Between 3 and 4 atmospheres the current was stopped and the cell was short-circuited for about one and one-half hours, but this did not seem to have any noticeable effect on the subsequent observed readings.

Although this experiment was made about seven years ago, and has been described to a number of electrochemists and physicists, no complete explanation has so far been suggested by any of them. Want of time for pure research work has prevented Mr. Reed as well as the author, from carrying on the investigation further, but it is hoped that the present description, which is the first one published, may lead some one who has the time and the facilities, to make such further investigations as will show where the discrepancy lies.

It has been suggested that possibly some of the oxygen and hydrogen pass mechanically from one electrode to the other by being dissolved or suspended in the liquid owing to the great pressure; and that these gases on their arrival at the opposite electrodes from which they came, partially "depolarize" them, thereby lowering the voltage. This was quite possible, as the electrodes were necessarily very close to each other, and there was no diaphragm between them. Lorenz found a similar result in the electrolysis of fused salts; a sort of cloud formed around one electrode, and when this cloud extended over to the other electrode the voltage fell; that is, the product formed at one electrode seemed to act as a depolarizer when it came in contact with the other electrode.

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Under this assumption the amount of oxygen corresponding to Faraday's law, may be said to be divided into three parts; one part goes off as free gas; the second remains suspended or dissolved in the water and gradually finds its way to the cathode where it combines electrochemically with an equivalent amount of hydrogen which tends to be generated at that electrode; the third part combines at the anode with an equivalent amount of hydrogen which has similarly been brought over mechanically from the cathode in suspension or in solution; this third part is not really set free as oxygen gas, as it combines at once with hydrogen, but it must of course be included in the total amount as calculated by Faraday's law. The hydrogen at the cathode is likewise assumed to be divided into three such parts just like the oxygen. Faraday's law is therefore satisfied.

If there is such a partial depolarization by the gases themselves, the following might be a possible explanation, neglecting for the sake of simplicity the energy which is still confined in the compressed gases. This explanation, however, is intended to account only for the final or total results, and to show that they are not inconsistent with the law of the conservation of energy; and no attempt will here be made to explain the detailed intermediate steps, nor to discriminate between primary, secondary, temporary, or intermediate reactions, as that would involve too much speculation. The important thing is to show that the ultimate results are not inconsistent with well established theories.

If some of the gases which tend to be generated, combine again in this depolarizing action, as explained above, it follows that there will be less *free* gases than would correspond to Faraday's law; or in other words a gram of *liberated* gases would then correspond to more ampere-hours or coulombs than would be required by Faraday's law. But to decompose the gram of water, from which these free gases were formed, requires a known and definite amount of energy in joules; dividing this number of joules by that number of coulombs, gives the volts required to produce this amount of decomposition. Now as this total number of coulombs was *more* than is required by Faraday's law, it follows that the voltage must be *less* than required by Thomson's law, as their product, which is the amount of energy of decomposition per gram, is a fixed quantity.

To illustrate this with a numerical example, if nine-tenths of

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the ions corresponding to Faraday's law, combine again with the gases to form water, as described, the other tenth which is liberated as free gas, will correspond to ten times the total ampere-hours required by Faraday's law; hence, there must be accounted for only one-tenth the voltage corresponding to the combination of Faraday's and Thomson's rules, as the product must remain the same.

This, it will readily be seen, is nothing more than a direct calculation of the voltage from the energy of the amount of gases actually liberated and the coulombs which have actually passed, that is, the number of volts is equal to the number of joules required theoretically divided by the observed number of coulombs; as Faraday's law is not involved in this calculation, it is not violated thereby. Moreover, this conception does not contradict Faraday's law, as it is assumed here that all the ions corresponding to it actually took part in the reaction, but a part of them recombined again with some of the gases so that only a part were permanently set free as gas. Those that recombined may be said to have given their energy back to the system, which in some way must have contributed to lower the total voltage required.

If this is the correct explanation, it follows that the amount of gas permanently liberated per ampere-hour diminishes rapidly as the mechanical pressure increases; and that at 15 to 22 atmospheres the recombination proceeds almost as fast as the decomposition, in this particular apparatus. This may well have been the case. It could probably be determined by repeating the test with a diaphragm between the electrodes to prevent the gases of one electrode from getting to the other, in which case probably totally different results would be obtained.

The experiment above described suggests another. Suppose a closed vessel, of sufficient strength, to be filled completely with acidulated water and provided in the inside with electrodes, what would take place when a current is passed between the electrodes? If the water were imcompressible and the vessel inexpansible, and if there is no recombination of the gases, the pressure should rise instantly to 1865 atmospheres and would not increase beyond this, no matter how much gas was generated, as the gases would have to occupy the same volume as the water from which they were formed. If the explanation offered above

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for the original experiment is correct, the gases would probably soon recombine about as fast as they were being generated, in which case there would be little further change.

DISCUSSION.

MR. H. RODMAN: Mr. President, I have experimented a little with such aqueous electrolysis, using constant electrodes, and have been able to electrolyze certain solutions indefinitely. The electrolysis was continued for about two weeks without change in either electrodes or electrolyte while the pressure was only about three- or four-hundredths of a volt. Apparently there was depolarization at both poles. It seems very probable that it was the same thing that happened here.

MR. W. MCA. JOHNSON: This is as beautiful a case of theory and experiment harmonized as I have ever seen. The two gases, as is quite apparent, and as Professor Bancroft showed me, are actually mutual depolarizers. The combination of the oxygen with the hydrogen at one pole and the oxygen and the hydrogen at the other affects the solution pressure of each. Consequently the volume of gas produced is not that in accordance with Faraday's law.

DR. H. S. CARHART: I should like to call Mr. Hering's attention to the fact that Faraday's law is not one involving voltage at all, but current only, or quantity of electricity. Therefore, the only way to settle a case of this kind, and say whether it antagonizes Faraday's law, which I do not believe, is to measure the quantity of electricity which goes through and the quantity of the gas electrolyzed. The other question of low voltage, it seems to me, is entirely independent of Faraday's law.

MR. REED: I agree with Dr. Carhart that Faraday's law has nothing to do with the voltage. I would like to ask Mr. Hering how the insertion of a diaphragm there would settle the question. If it is only to separate the two products, the diaphragm would not accomplish anything, because the products being gaseous would mix in the space above the diaphragm, and then would be easily dissolved on both sides. I do not see that that would settle anything at all. The argument that has been made by many, and which is shown here, is that the substances formed at

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one electrode passes over to the other and become depolarizers; that is to say, we finally have a strong solution of oxygen and hydrogen on one side, and the same solution of oxygen and hydrogen on the other side. The current, therefore, at the anode uses up dissolved hydrogen, and the cathode uses up dissolved oxygen and so produces no gas. That would account perhaps for a current passing with the production of no gas; but in this case we have the production of gas at both poles. Now, suppose we admit that a certain fraction of the current, say ten per cent.—or twenty or thirty—is used in oxidizing dissolved hydrogen at one pole and reducing dissolved oxygen at the other. That fraction of the current, of course, would produce no gas; and we can easily see that that fraction of the current would not require any electromotive force, theoretically. But I do not see how that explains the fact that the other fraction of the current which evolves hydrogen at one pole and oxygen at the other, can perform that chemical separation with an electromotive force of one-third of a volt. It seems to me that whatever fraction of the current uses up dissolved oxygen and dissolved hydrogen will do so in accordance with Faraday's law; but that will account only for that fraction of a current. The rest of it which does not perform that electrochemical reaction, but performs the electrochemical reaction of liberating oxygen and hydrogen, must also act in accordance with Faraday's law, and must require an electromotive force equivalent to that of the chemical energy involved.

How two gases can be "actually mutual depolarizers," as Mr. Johnson says, and, by acting as such, cause these two gases to be evolved without requiring the energy of separation or the corresponding voltage, is not apparent.

MR. R. S. HUTTON: In relation to the last point raised by Mr. Reed, it might be of interest to mention that during the last few months some work has been carried out by Chapman and Lidbury, in the electrolysis of water vapor at ordinary temperatures. This water vapor has been electrolyzed by a fairly high voltage current, and curiously enough one obtains from four to six times the decomposition which is calculated according to Faraday's law. I do not know if that will help us to explain this process, but it seems interesting in connection with this subject.

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MR. REED : It seems to me that that is another phenomenon which requires explanation. I do not see that it explains this phenomenon.

PROF. C. F. BURGESS : It seems to me that the construction of the apparatus may have something to do with this phenomenon, especially in view of some experimental work done in France five or six years ago. In the experiments of Cailletet and Collardeau, sulphuric acid was electrolyzed with platinum electrodes under high pressure, amounting to three or four hundred atmospheres. This work is referred to by Dr. Palmer in his book, and possibly he can give us the exact reference. But the phenomenon observed there was not the same that has been observed by Mr. Hering. The electromotive force rose there instead of decreasing. This was shown by a number of discharge currents. The platinum plates acted as an accumulator and the discharge currents given show a higher electromotive force as the pressure is increased, and also show an enormous increase in capacity, due to the absorption of the gas at the electrodes. This is especially so if spongy platinum be used ; and the capacity is given in that paper as a great deal higher per kilogram of electrode than obtained in the best and latest storage batteries. This storage of the products of electrolysis may have some influence on this phenomenon.

I have performed certain experimental work along this line, enclosing an electrolyte in a very strong steel tube, and have found that the electromotive force of decomposition would increase or would decrease with the pressure, depending on the electrodes that were used, on temperature, etc., and that there were certain other factors to be taken into account. I think one factor is the different action of the electrodes under different pressure.

I should like to ask Mr. Hering if he has calculated the theoretical increase which we should expect for the increase of pressure of an atmosphere.

DR. W. D. BANCROFT: Some experiments have been made by Professor Haber which furnish an analogy to this. If you electrolyze a solution of sulphuric acid or caustic potash between platinum electrodes and work with a given current density, it takes a given voltage. If you add nitrobenzene to the solution,

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the nitrobenzene is reduced and the voltage drops. If the current density is low enough and the solution is properly selected, you can get it so that no hydrogen is set free at the cathode at all. If the current is too high you will get some hydrogen evolved. In other words the nitrobenzene acts as a perfect or as an imperfect depolarizer depending on the conditions; but in either case the voltage is lower than if there were no nitrobenzene. The case cited by Mr. Hering is broader in a way because we have a depolarizer both at the cathode and anode. This is, of course, merely a restatement of Mr. Hering's argument, with which I agree. The further proof is the one cited by Mr. Burgess in the experiments by Cailletet and Colardeau and by Guilbault, where the hydrogen and oxygen were separated, but under high pressure, a higher electromotive force was found and the increase agreed within the limits of experimental error with the theoretical value due to the change of pressure. Here we do not get that corresponding result, but we have the difference that the hydrogen and oxygen are not kept separated, and the result is exactly the one we expect; we have an imperfect depolarizer, both at the anode and cathode, and get a lower voltage and an evolution of gas at both electrodes.

I should like also to call attention to an interesting experiment, which would probably give the same result, made by Foerster and Seidel, in Germany, where they worked with solutions of copper sulphate at a temperature of 100°. By arranging the concentration and current density properly, there was neither evolution of hydrogen at the cathode nor precipitation of copper. In other words, the copper that should be precipitated was at once dissolved again by secondary action. I have no doubt that, if they had measured the voltage in that particular case, they would have found it lower than in the case where the copper was actually precipitated.

DR. LOUIS KAHLENBERG: It seems to me the explanation given by Prof. Bancroft is a plausible one, especially when we remember that the solubility of these gases is largely increased by the increase of pressure.

I should like to ask Mr. Hering about how long this experiment lasted, and whether he had an ampere-meter or voltameter in the circuit.

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MR. HUTTON: It would be interesting to know whether Mr. Hering has tried any other metals besides platinum, for the electrodes. It seems to me the curious results obtained by Caspari might give us indications in this case. We have in Caspari's experiments the lowest decomposition voltage with platinum or palladium, and in just these cases the hydrogen is much more soluble. This low voltage has been explained by the actual atom going into the metal, and the ease of separation being facilitated in the case of platinum and palladium by the actual solubility of the hydrogen in the metal. Now, it seems to me that under higher pressure the solubility of these gases would be greatly increased in the case of platinum and that might, to a certain extent, explain the difficulty. It might be explained by other theories, but the solubility would be much greater under higher pressures, and therefore the separation might take place with more ease, and the decomposition of the water possibly be carried out under a smaller voltage, than under pressure of the ordinary atmosphere.

DR. F. HABER: Mr. Guilbault (*Comptes rendus*, 1891) found that there is perfect agreement between the theory of the electromotive force in the oxygen-hydrogen cell at different pressures, and experiment. According to the theory, the electromotive force of this cell must increase with increasing pressure, and he showed that this increase really takes place. Considering this fact it seems to me that the experiment of Mr. Hering can only be explained as Mr. Hering did in connection with the results of Professor Lorenz, by considering the effect of interfering convection currents.

PRESIDENT RICHARDS: This experiment is a paradox, if on passing the current there is obtained an amount of oxygen and hydrogen proportional to Faraday's law. In that case, certainly, the recombination of the oxygen and hydrogen would give us more energy than the electrical current had supplied. Two or three considerations will have to be investigated primarily. The first would be a quantitative experiment, to see whether the amounts of oxygen and hydrogen are proportional to Faraday's law. I do not believe that they can be. Secondly, an experiment to determine if the amount of oxygen and hydrogen are in the same proportion as they are in the water. If not, then there

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is some chemical change in the electrolyte, and since the electrolyte was dilute sulphuric acid, the possibility of the formation of other acids, as persulphuric acid, must be taken into account. A consideration of those two facts, besides the increased solubility of the gases and their recombination, might also help to explain the paradox.

MR. CARL HERING : Mr. Chairman, Mr. Rodman's experiment simply confirms this one, as he seems to have gotten the same results. I believe that if our experiment had been continued with a stronger tube, there would have been a point at which a stationary stage would have been reached, in which the current would pass through the electrolyte without causing any resultant decomposition. This is referred to in the paper itself.

Professor Carhart must have misunderstood me, for as my paper shows, I did not say that Faraday's law involved the electromotive force. I am well aware of the fact that it does not, and the paper will show this. Faraday's law is satisfied in this experiment, notwithstanding the small amount of gases which actually result, if we assume that the gases are really set free according to Faraday's law, but afterwards recombine again in part. Just as in the experiment of Lorenz with the fused salt, the proper equivalent is produced according to Faraday's law but some of the product gets over to the other electrode and there depolarizes and thereby gets back into the solution again. Faraday's law may therefore be said to apply in this case even though the actual amount of gases set free do not seem to correspond with the law.

Mr. Reed asks why I thought the insertion of a diaphragm will change the results. If a diaphragm were inserted between the two electrodes then the oxygen and hydrogen which seem to be suspended mechanically in the liquid, could not get over to the opposite electrode, and would not therefore act as depolarizers. I believe that if the two electrodes are thus separated so that this depolarizing action cannot take place, the curve will be reversed and will then correspond with the results of the researches that have been mentioned in the discussion.

Professor Burgess asked for the theoretical increase. I do not understand what he means. I calculated the following : If a given volume of water is completely decomposed without chang-

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ing its volume the pressure will be 1865 atmospheres. Perhaps this figure will give him the information.

PRESIDENT RICHARDS: If you will allow me to interrupt—I made the calculation that the voltage should increase 0.01 for the first additional atmosphere pressure, and to 1.83 volts if the gases occupied the volume of the water.

MR. HERING: I tried to make this calculation, but I was unable to find out whether the voltage, calculated by Thomson's law, includes the energy of expansion or not; that is, the energy which corresponds to a gas expanding to 1865 times its original volume. There seems to be a question whether this energy comes from the electrical energy of the current or from the heat of the solution. If it comes from the current then the voltage should vary with the pressure; if it comes from the heat of the solution, then the voltage should be independent of the pressure.

Concerning the remarks of Professor Bancroft, I would like to add that in talking about this experiment with him, about a year ago, he made the suggestion of the solution of the gases, which then led me to the explanation which I have offered.

Professor Kahlenberg asked how long the experiment lasted and whether we had a voltameter in circuit. I do not remember how long it lasted, but it was not more than a couple of hours; we had no voltameter in circuit, only an ammeter. We simply passed a constant current between the electrodes, measured the voltage and read off the gas pressure every now and then. I do not remember what the current was, but it was only a fraction of an ampere. During part of the experiment the two electrodes were short-circuited as described in the paper.

Mr. Hutton asked whether we tried it with any other metals. There was only a single experiment and that was with ordinary platinum wire electrodes.

In conclusion I want to emphasize the fact that I do not consider Faraday's law violated in the least.

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Abstract of a paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 17, 1902, President Richards in the Chair.

ELECTROCHEMISTRY AT THE WORLD'S FAIR, ST. LOUIS.

By W. E. Goldsborough.

At St. Louis there is in process of development an International Exposition in which this Society can not but be deeply interested. It will be brought to completion and presented for the education of the people of our country and the world at large, just at the time when the electrochemical industries of America will be acquiring that strength which will make them a most important element in our national life. Already I have heard it said by more than one distinguished foreigner that America is regarded as having gained an unimpeachable position and prominence in the building up of this new industry, and I cannot but think our Society hears these admissions with no small degree of pride and satisfaction.

To my mind it is right and highly desirable that an intimate knowledge of conditions should exist between the electrochemists and the officers of the exposition. By the officers of the exposition I am commissioned, not only to extend to you a hearty invitation to participate in their great undertaking, but to go further and assure you that in a most helpful spirit they extend to you assurances of their great desire to place the resources of the exposition at your command to the end of picturing, in a way that will attract international attention, the true worth and vigor of this infant industry.

In accordance with the provisions of the official classification of the exposition, the products of the electrochemical processes will be shown in several of the exhibit buildings. Manufacturers, liberal arts, machinery, and mines and metallurgy, as well as electricity, come in for a share in these products. And indeed, it will be proper to exhibit certain electrolytic processes in the palace of liberal arts, and certain others in the palace of mines and metallurgy; but to electricity, in unrestricted measure, is accorded the privilege of giving expression to all electrochemical

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operations, whether purely electrolytic in character, whether brought about by electrothermic means simply, or whether attained by a combination of electrothermic and electrolytic methods.

In the department of electricity one of its five groups is entirely devoted to electrochemistry.

Class 434 of this group is devoted to primary batteries and storage batteries. In this class, in addition to an exhibit of the finished products, efficiency tests of batteries will be inaugurated and a careful record kept of their performance during the period of the exposition. In addition to these, processes in the manufacture of various types of storage batteries will, it is hoped, be arranged for in order that this matter may be pictured in a broad way.

Class 435 embraces electrolytic appliances and processes. All forms of electroplating, methods of electrotyping, and finally and most important, the applications of electrolysis in the reduction of ores and other related work find place here; that this class presents the possibility of a most interesting and instructive series of exhibits will be at once recognized. Electrolysis plays an ever greater and more important part in the business of the world each year. It has attained to a well recognized position. Yet, with increasing emphasis, the work we see about us here at Niagara Falls demands for it an ever broader and more important recognition.

Class 436 deals with electrothermic appliances and methods, and, therefore, includes all of the electric furnace applications which we have found pictured in the great local factories on such a large scale. Nothing is more impressive than an inspection of the actual work of the electric furnace. We are, in fact, almost appalled in noting the wonderful results, both in magnitude and industrial importance, which are brought about by the dissipation of electric energy by these means and its transformation into heat. The electric arc, when applied on a large scale, attracts and rivets the attention not only of the initiated, but the uninitiated as well. It presents the picture of power in a most fascinating way.

Class 437 deals with the application of electricity to industrial chemistry, disinfection of sewerage water, manufacture of bleaching-powder, caustic soda, nitric acid, chlorate of potash, etc., etc. Much can be done to make the exhibits in this class of great

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value and interest, not only to students, but to engineers and chemists. Some of the most interesting electrochemical operations find expression in the field of industrial chemistry, and a strenuous effort will be made to show all of its important divisions.

With the brief outline that I have given you, you will begin to appreciate the immensity of the task which is set for those servants of the exposition who will bring to its full realization the hope which I entertain for the success of the electrochemical group. That all the help and assistance which you as electrochemists can offer us will be most acceptable and gratefully received, it is hardly necessary for me to say. That I ask it, is because I believe you are as deeply interested as myself in having an adequate picture of what you are doing presented to the world. In my judgment, a large and fine exhibit in this group will have a most beneficial effect upon the development along electrochemical lines. If, to-day, the financiers and people of the country generally had great confidence in the ability of electrochemists to carry to a successful issue all that is rightly claimed for electrochemistry, and if "electrochemistry" had become as much of a household word among our people as have the technical terms employed in the older and better known branches of industry, it is safe to say that the money which will be investing in and about Niagara Falls within the next few years, would from the very force of the confidence of the general public, be augmented many fold. We, at the exposition, are not, therefore, attempting anything that is illogical or unreasonable, when we plan to show all of the electrochemical processes I have mentioned in actual operation, and to show as many of them as may be possible on a commercial scale.

In the electricity building, as you doubtless know, space will be free to exhibitors, and provision has been made to supply exhibitors with free power, within reason. The installation facilities are also all that can be asked, inasmuch as the railroad lines will be extended right into the electricity building during the period of installation, and traveling cranes and movable hoists will be provided over all of the principal aisles in the building.

At the present time the success of the exhibits in the electricity department can be said to be assured, inasmuch as a large number of most interesting working exhibits have already been

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arranged for in the allied branches. A maximum load of 2,000 horse-power will be available for the development of the working exhibits, and without doubt the building will teem with light and activity.

Within the next two years we will have time to give the topic which has been the subject of my talk the careful attention and thought which it needs, as well as the strenuous effort and labor which its development deserves. From the interest you have been good enough to manifest in what I have said, I feel assured of your helpful co-operation and advice in this very important department of my work, and I hope I have not led you to expect anything that will not be fully realized.

In closing I wish to say that the Chief of the Department of Mines and Metallurgy has extended to you through me the most cordial assurances of the interest which he takes in this work. It is his desire that in all its details the applications of electricity to metallurgy shall be given the fullest expression.

DISCUSSION.

MR. HERING: Mr. President, the object of our Society is to promote the interests of electrochemistry, and it seems to me that we can aid in doing this by encouraging Prof. Goldsborough's efforts in having electrochemistry made an important feature of this exposition. I therefore offer the following resolution:

WHEREAS:—The American Electrochemical Society in convention assembled recognizes the great international importance of the Louisiana Purchase Exposition, and feels that it will do much in placing before the peoples of the world a true picture of our national progress, and

WHEREAS:—In no branch of our scientific or industrial progress have greater developments taken place recently than in the field of electrochemistry, therefore be it

Resolved:—That the American Electrochemical Society hears with great satisfaction the announcement that steps are being taken looking to the organization of a fine and comprehensive exhibit in the group of electrochemistry, and offers assurances of hearty good-will and cooperation in the accomplishment of this much-to-be desired end.

DR. H. S. CARHART: Mr. President, I rise to second this resolution with very great heartiness. I am a believer in expo-

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sitions. My experience in expositions has run over a longer period than that of any one here, except perhaps Dr. Keith, beginning with the Exposition of Electricity in Paris in 1881, where I happened to be one of the International Jurors for the United States; and that exposition marks an important epoch in the history of electricity. I do not know that the exposition at St. Louis will be equally important in that regard, but since I understand there is to be an Electrical Congress, and that specialties in electrochemistry are to be introduced and exhibited, it is of great importance to this young society that we should, by our united efforts, encourage the undertaking which Professor Goldsborough, one of our members, has in hand. I repeat, therefore, that I have very much pleasure in seconding this resolution.

MR. H. B. COHO: Mr. President, taking Professor Goldsborough's remarks in good faith, as I know we all do, when he claims that electricity is going to be the prime mover, and all other sciences be subsidiary to it at the St. Louis Exhibition, it seems to me that this is the time for all electrical engineers and others to give Professor Goldsborough our earnest support and help him to make the Department of Electricity not only an illustration of what has been done, but also indicate as much as possible what we hope will be done with electricity and in electrochemistry.

The day has passed when a number of machines sitting around nicely painted will impress the general public.

In seconding Professor Carhart's remarks I only want to say that I believe Professor Goldsborough intends to make the Department of Electricity the leading feature of the St. Louis Exposition, and that we can all aid our own branches of electricity by giving him our earnest support.

The motion being put to a vote was carried without dissent.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 17, 1902, President Richards in the Chair.

THE ELECTRONIC HYPOTHESIS AND ITS APPLICATIONS.

By Arvid Reuterdahl.

Science, like history, repeats itself. The repetition is not, however, along a perpetually reiterating curve like the circle but along a continually ascending circular spiral. There is advancement along with the repetition.

To be more specific, we to-day possess considerable knowledge concerning the outward mechanism of the world. We have now come, however, to a point where a better understanding of the world's outward mechanism depends entirely upon the acquisition of more learning concerning its inner mechanism.

Even the tiny atom does not seem to be minute enough in its dimensions to satisfy the needs and necessities of science, and it is consequently subjected to a process of subdivision which results in producing a large number of excessively small particles or corpuscles having properties and activities foreign to the atom as a whole. The atom as known to chemistry is according to this notion a conglomeration of a large number of these peculiar corpuscles. Each atom is then somewhat analogous to a small solar system consisting of numerous planets and myriads of stars. Science further endows these small corpuscles with definite electrical charges and with the ability to sever their connections with any one particular corpuscular group or atom to attach themselves to another group according to the definitive dictation of prevailing conditions. We have already discarded entirely the Newtonian corpuscle and the emission theory, and are we reading too much into this modern movement if we discern therein a tendency to abandon also the illusory scientific theory of the ether, that fantastical waste-basket for all the chimeras of higher mathematics?

Great interest has recently been shown in those peculiar phenomena known as cathode rays, Röntgen rays, and Becquerel rays.

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The ardent investigation of these subjects has been fruitful in giving to the world the so-called "Electronic Hypothesis." It is our present purpose critically to consider the value and meaning of this hypothesis and its applications.

A brief sketch of the electronic hypothesis will better enable us to understand and estimate its significance. J. A. Fleming has ably set forth the main postulates of this hypothesis in an article entitled "The Electronic Theory of Electricity." We take the liberty of making a short abstract of the essential matter contained in this article.

The modern electronic hypothesis is the offspring of the phenomenon of so-called "radiant matter," which was thought to be a form of matter differing considerably from the usual forms, the solid, liquid, and gaseous. The phenomenon of "radiant matter" can be observed in an ordinary vacuum tube having its terminals connected with an electrical device such as an induction coil. When the circuit of such an apparatus is closed, a stream of extremely minute particles of matter charged with negative electricity will be sent forth from the cathode terminal of the tube with enormous velocity. Sir William Crookes, the pioneer in this field, showed conclusively by numerous experiments that these small electrically charged particles possessed the ordinary properties of matter in that they are able to propel small vanes inserted within the tube. To these small charged particles J. J. Thomson has given the name corpuscles; and by a series of brilliant investigations he has shown that their velocity is from one-fifth to one-third that of light, and that their mass is about one one-thousandth of the mass of an hydrogen atom.

It has also been shown that although the mass of these tiny corpuscles is only about one one-thousandth of the hydrogen atom, yet they carry a charge of negative electricity equal to that carried by the entire hydrogen atom. The amount of this charge, which has been called "one electron," can be calculated when it is known that 96,540 coulombs are necessary to electrolyze one gram of hydrogen at 0° C., and 760 mm. of pressure, and that 11,200 cc. of hydrogen weigh one gram, therefore we see that 8.62 coulombs are sufficient to evolve one cubic centimeter of hydrogen under these conditions. The number of hydrogen atoms in 1 cc. at the specified conditions has ap-

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proximately been determined as 4×10^{19}. All that is necessary then to find the electrical charge on one atom of hydrogen is to divide the total electrical charge necessary to electrolyze 1 cc. of hydrogen by the number of hydrogen atoms per cubic centimeter. When this operation is performed we get a quotient of $\frac{21.55}{10^{20}}$ of a coulomb. To change this result into C. G. S. electrostatic units we multiply by 3×10^{9}. This gives a result of $\frac{64.65}{10^{11}}$ of a C. G. S. electrostatic unit. As the amount of the negative charge existing upon one of the corpuscles is equal to that existing upon the hydrogen atom, the above result holds for both the hydrogen atom and the corpuscle.

No experimental evidence has yet been found which shows that this electrical charge of "one electron" can be separated from the corpuscle itself. Generally speaking it is no more possible to separate the electronic charge from the corpuscle than it is to separate momentum from moving matter. The corpuscle itself can then for all purposes be considered as constituting what we ordinarily call negative electricity.

Radiant matter, cathode rays, corpuscles, and electrons are then the same thing.

Very interesting discoveries concerning the behavior of these corpuscles have been made. It has been found that they can pass through thin metal windows inserted in the vacuum tubes, thus getting into the space beyond without in any way losing their identity.

The very interesting phenomena of Röntgen rays and the peculiar emanations known as Becquerel rays, which originate from such radio-active substances as uranium, thorium, polonium, radium, and actinium, are similar in every respect to the phenomenon of radiant matter or cathode-rays, and consist of streams of negatively charged corpuscles moving with great velocities. Observation has shown that such rays are deflectable by a magnet. Becquerel has shown that the ratio $\frac{e}{m}$ of the charge to the mass of these negatively charged corpuscles is about 10^{4}. About this same ratio value holds good for the cathode-rays produced in vacuum tubes.

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According to the electronic hypothesis the atom is capable of subdivision into two parts of very unequal size. One part consists of the minute negatively electrified corpuscle already described, which is absolutely identical in its nature without regard to the kind of chemical atom from which it owes its source. The second portion of the atom is positively electrified and is much larger than the first portion. This positively electrified and larger portion of the atom corresponds in its nature to the particular chemical type of the atom from which it is separated. The positive portions then seem to give the chemical characteristic to the entire atom, and consequently they vary in their nature as widely as the chemical natures of the atoms themselves.

The electronic hypothesis imagines the atom to consist of a number of concentric shells of electrons alternately negative and positive. The external shell is thought to consist of negative electrons. The difference in the aggregate number of negative and positive electrons gives us the chemical valency of the atom. The hydrogen atom regarded from this point of view would consist of from 700 to 1000 negative and positive electrons arranged in the manner described.

In a neutral condition the outer shell of the electronic atom consists of negative electrons enclosing an inner kernel or group existing in such an opposite electrical condition that if one negative electron be removed from the atom the same is left in a positive electrical condition. Be it remembered at this point that when we speak of detachable electrons we mean the negative electron. Although positive electrons undoubtedly exist, yet up to the present time they have not been isolated. The negative electron corresponds to what is commonly known as the negative ion, while the neutral atom minus a negative electron corresponds to the ordinary positive ion.

The above gives us a general synopsis of the main theses of the electronic hypothesis.

The electronic hypothesis can be applied to the explanation of all the diverse phenomena of electricity. In the light of this hypothesis, the electric current consists of the motion of electrons. A conductor of electricity is a body within which electrons are capable of moving. If an electromotive force is applied to a conductor the electrons begin to move. The conductivity of every substance depends upon the ease with which the electrons

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can make their way through the molecules, and this would in turn depend upon the complexity of the molecules.

Electrons in rotation produce the known magnetic effects. Space does not allow us to go further into particulars. The "Electronic Hypothesis" certainly seems to have latent possibilities which are dazzling. It seems to be far-reaching in its scope and flexible in its applications. The writer fears, however, that dangerous and fatal oversights have been made by the formulators of this hypothesis which must be rectified, if possible, or otherwise the hypothesis will not be able to withstand sharp and critical analysis and will consequently fall to the ground.

Modern science has heretofore assumed the existence of two entities in the world, matter and energy, the one just as indestructible as the other. Science sharply differentiates these two notions. Properties and qualities which can be assigned to one of these entities cannot necessarily be indiscriminately ascribed to the other. A given quantity of matter is said to contain a definite and measurable mass. Now it would be absurd to speak of a certain amount of energy possessing a mass of measurable magnitude. It would be equally absurd to attempt to apply the universal law of mass attraction to various quantities of energy. Matter seems to be the vehicle by which the transportation and exchange of energies is effected. It may be likened to a delivery wagon which transports various useful commodities from one place to another. Such a wagon need in no way be affected by the giving up or taking in of new commodities. Similarly no change need be made in the magnitude of a given mass because a transfer or transformation of a certain amount of energy has taken place in it or by means of it.

Hitherto we have been accustomed to regard electricity strictly as a form of energy. An enormous aggregation of conclusive evidence has positively demonstrated that it is possible to transfer electrical energy from one body to another without in any way affecting the mass of the two bodies concerned. This very fact is used time and again in order to illustrate the vast difference between the removal of a given amount of energy from a particular body and the removal of a portion of the mass of the body. If a certain amount of the mass of the body were removed, we could immediately ascertain this amount by resorting to the process of weighing, but gravitational methods are absolutely futile

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when we are dealing with energy. Indeed, one of the first and most universal differences recognized between matter and energy is this very fact that matter possesses weight and energy does not. When we say that matter possesses weight, we mean, of course, that a definite and measurable amount of attraction is observable between given masses.

Let us now apply these considerations to the tenets of the electronic hypothesis. As we have already seen, this hypothesis considers the transfer of electrical energy in all of its manifold and diverse aspects to consist of the transfer and interchange of minute material corpuscles called electrons. The mass of these minute particles is, of course, extremely small, being about one one-thousandth of the mass of the hydrogen atom. Like an expert in legerdemain the hypothesis adroitly causes you to overlook what is taking place in the left hand by making a clamorous demonstration with the right. The conjuror shows us that in his right hand one electron carrying $\frac{65}{10^{11}}$ of a C. G. S. electrostatic unit of electricity is being transferred from one body to another, but he desires us to ignore absolutely what is simultaneously and necessarily taking place in his left hand; that is, the corresponding transfer of a genuine portion of matter having a measurable mass equal to one one-thousandth of the mass of the hydrogen atom. In his right hand one body gains precisely the amount of electrical charge which the other loses, while in the left hand, as our expert must necessarily admit, the first body gains exactly the amount of matter which the other loses. Consequently our ordinary mass comparator, the balance, should show us at once if the transfer of this electrical charge is simultaneously accompanied by a proportionate transfer and consequent change in the masses of the two bodies. Not a single instance of such a change in the mass of a body due to the change of the magnitude of its electrical charge can be found in the entire realm of scientific observations, a circumstance which certainly leaves the electronic hypothesis in a most perplexing situation.

For the present we will leave the theory to its own fate while we take up some other vital considerations which may possibly throw some valuable light on the hypothesis under review. We are accustomed in considering electrical phenomena to speak of

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positive and negative charges of electricity. The terms positive and negative are, of course, nothing but arbitrarily selected mathematical terms used to signify the fact that the electrical charges which are met with in experimental investigations are opposite in their nature. In connection with our consideration of electrical charges we often speak of the force of electrical attraction or repulsion existing between electrically charged bodies. Now so much mysticism exists concerning what force in general really is and its relation to matter that it becomes necessary to go into detail concerning this point. We hope that this consideration will be specifically fruitful in bringing to light certain logical necessities which must be incorporated in our view of the electronic hypothesis in general, and which also may possibly give a new and broader meaning to the notion of force as manifested in electrical attraction and repulsion.

To give a satisfactory definition of force is very difficult. Possibly the following definition may cover the case: Force is the result which is qualitatively and quantitatively determined, and which must or may occur, whenever any given element enters into a specific relation with any other.

If we logically analyze the implications involved in the fact that a given quantity of matter possesses fixed limits of extension, we arrive at the general idea of two opposite forces. An attraction of the separate parts of the matter must exist which, if allowed to work unhindered and alone, would reduce this extension to zero. Similarly we are obliged to assume a repulsion which, if it were the only agent acting, would make the extension infinite. This logical analysis can be applied to the idea of any body which has definite magnitude. Whatever the component elements of the world may be, they cannot be regarded as governed by the mere abstract principles of attraction or repulsion which would drive the elements continuously into or out of one another. On the contrary, the law which governs the activities of the elements constituting the world must be one which aims at the conservation of the whole order, and which at each and every moment of time assigns to them their particular place. It is that force which proceeds from the sum total and aggregate mass of the elements which assigns to them their position. It is this force which, although it appears to reside in each individual element, nevertheless acts as a corrective against any deviation

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from the fundamental law imposed upon the whole. It is this force which sets definite boundaries to the remoteness or nearness of objects in relation to each other. In the first case, it appears as a force of attraction, while in the second case it seems to be a force of repulsion. This function of self-conservation, which is the fundamental principle of activity of an individual thing, we logically analyze into two principles of attraction and repulsion. The real fact of the case is, however, that self-conservation is secured by adopting whichever mode of activity—either that of attraction or of repulsion—happens to be dictated by the conditions which prevail at that particular instant. Furthermore, any tendency to return to equilibrium regarded as a phenomenon in space will inevitably appear in the very simplest possible form. The simplest principle into which such a tendency can be analyzed is that of approximation and separation of the elements considered. It is, therefore, both customary and logical to represent all physical processes as consisting merely of motive forces of attraction and repulsion.

Our logical analysis of the implications of phenomenal existence in space therefore leads us to think that the only satisfactory representation of the activities of things is by postulating two component forms of activity, that of attraction and that of repulsion. Both of these forms of activity must be interpreted as being our logical representation of a more general and universal principle of interaction. In a previous paper on the "Atom of Electrochemistry," the writer represented this law of interaction by the formula

$$S = f(u, v, w \ldots\ldots\ldots\ldots R).$$

The principle of self-conservation, being a logical implication of the very notion of existence itself, demands that any working hypothesis or formula which shall do justice to the actual processes and activities of things shall embody within itself the two notions of attraction and repulsion. Consequently we are forced to substitute for the law of gravitation some other principle which contains within itself the two ideas of attraction and repulsion. If this is done, and it must be done, we shall then possess a means of obviating the contradictions which we have already seen are contained in the electronic hypothesis.

The writer of this paper has come to the conclusion that there

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is a principle which will enable us to remove the contradictions pointed out in the electronic hypothesis. The principle to which we refer is the electrical law of inverse squares, which states that the force of attraction or repulsion is directly proportional to the product of the two quantities of electricity on the bodies and inversely proportional to the square of the distance between them. This law holds good both in the field of electrostatics and electromagnetics. Those attractions which we have hitherto explained as coming under the law of gravitational attraction must, according to our present idea, be interpreted as being electrical phenomena of attractions. The electrical law of inverse squares does justice to both the principles of attraction and repulsion; and when coupled with the remaining concepts of electricity, it becomes an exceedingly strong instrument with which to cope with the wondrous facts which recent investigations constantly unroll before us. The principle contains absolutely everything that is found in the principle of gravitation and avoids all the difficulties. It is, undoubtedly, requesting a great deal to ask you so abruptly to give up such a venerable and time-honored theory, but applicability and validity is the standard by which all theories must finally be measured.

It has already been pointed out that the electronic hypothesis, in absolute contradiction to observed facts, ignores the gain and loss in mass which takes place in conjunction with, and is proportionate to the gain and loss of electrical charge. The amount of this transferred mass is measured in gravitational terms. If undeniable experimental evidence asserts that the balance indicates no gain or loss of mass corresponding to the gain or loss of electrical charge, we are left to choose between the horns of a dilemma; either the law of gravitation is for this case absolutely annulled, or the vast aggregation of experimental evidence, representing the combined result of the most careful and able experimenters the world has yet produced, which conclusively shows that interchanges and migrations of charged corpuscles do take place, is absolutely erroneous, invalid and worthless. Either we have discovered a grand exception to the law of gravitation, or we must cast to one side the brilliant researches of our best modern investigators. The "open sesame" by which the solution of the problem may be reached has already been suggested.

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If we substitute for the law of gravitation the more truthful electrical law of inverse squares our difficulties disappear. According to our present supposition the attraction existing between atoms, molecules, bodies, and the earth is electrical in its nature. We are in every case dealing with electrically charged bodies obeying the electrical law of inverse squares. The earth is then a conglomeration of electrically charged atoms and molecules, and may consequently be regarded as an enormous electrically charged sphere. It is to the earth's colossal electrical charge that we refer the smaller and minor charges existing upon masses near the earth's surface. It has been shown by J. J. Thomson that there is a definite connection between the dielectric constants of solvents and their dissociating power. He has also shown that similar relations hold good when molecules exist close to the surface of a conductor. These and similar considerations have caused the writer to formulate the following law:

The greater the electrical attraction between the earth and atoms or molecules near its surface the less will be the electrical energy necessary to disjoin and disintegrate the molecular structure.

Account must be taken of the valencies of the elements if the law is to be reduced to exact terms. If this is done we can restate the law in the following terms: The greater the chemical equivalence of the elements the less will be the ampere-hours per gram necessary to disjoin or disintegrate the molecular structure.

As a direct consequence of the above law, we can deduce a second law:

The number of electrons constituting one atom of a given element is strictly proportionate to the chemical equivalence of the element.

This law should enable us to determine with ease the number of electrons constituting any particular atom. All that is necessary then is to multiply the chemical equivalence of the element by some constant factor which must be determined by experiment. If we represent the number of electrons by n and the chemical equivalence by e, we can express the law by the equation

$$n = Ce,$$

where C is a constant quantity which must be determined from

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perience. If the number of electrons contained in the atom of any particular element were known, the value of the constant C could be found by simple substitution in the above formula. It happens that we have this requisite datum in the case of hydrogen. Within a reasonable degree of accuracy it has been determined that there are approximately 1,000 electrons in one hydrogen atom. The chemical equivalence of hydrogen being 1, we find, by substituting these known values in our formula, the value of C to be 1,000. By applying this formula to the other elements, the number of electrons in their atom is 1,000 times their chemical equivalent.

The time alloted to this paper does not allow us to go further into details.

The above brief examination has shown us that the electronic hypothesis entirely overlooks the fact that a transfer of an electrical charge from one body to another would necessitate a proportionate transfer and consequent change in the masses of the two bodies. That such a change in the masses of the bodies does not take place has been positively established by scientific research. We have seen, furthermore, that the logical analysis of the idea of force in general and of the force of gravitation in particular must include the notion of both attraction and repulsion. This demand is satisfied by the electrical law of inverse squares, which also fulfils the mathematical requirements of the law of gravitation. Hence, the electrical law of inverse squares should be applied to both gravitational and electrical conditions. Consequently the electronic hypothesis should be interpreted in the light of this broader law, and when this is done, the fatal error of the electronic hypothesis is obviated.

DISCUSSION.

DR. W. R. WHITNEY: Mr. President, this paper has called to my mind a little piece of work I have started. It is not complete, and so I do not want to say too much about it, but I think it may be of interest. Mr. Reuterdahl has called attention to the fact that, as he states it, "undoubtedly, charged electrons exist, but they have not been discovered yet." I have noticed that in looking through the literature, electrons are usually spoken of as nega-

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tively charged; we do not find positively charged electrons. Cathode rays are spoken of commonly, anode rays not so commonly, not as so well-known. It led me to perform some experiments, and while I am not as yet ready to publish results, still I am confident that in a luminous arc the material is usually carried as negatively charged particles. I have made some measurements, and have come to the conclusion that the mass of those particles, which J. J. Thompson stated in the case of hydrogen is a thousandth of the atom, may also be of that general magnitude in case of the metals. When we come to apply this to the carbon arc it becomes quite interesting. I believe in the cases of the carbon arc, the necessary passage of the material is also from the negative electrode to the positive.

MR. COWLES: A word as to gravitational potential. Take a mass a certain distance above the earth and lower it to the earth's level, and there is a loss of some of the potential energy stored in that body. Such difference is like the difference between the potential energy stored in a quantity of electricity when it is moved from a position of higher to lower potential. These cases of differences in potential can be expressed in terms of each other.

Newton recognized the necessity of a medium similar to ether, but he did not involve his mathematical calculations with the mechanical movement of such medium. The facts that he arrived at are nevertheless true. It does not seem to me that because a mathematician accepts the premise that force will act according to a law, through space, without a medium, that his conclusions are necessarily vitiated. While some unknown function may alter the law of gravitation when we pass down to molecular distances, I am inclined to think that it still acts in the same manner as we know the law, and that the force in relation to the masses involved, becomes greatly magnified. If this view is correct, speculation such as Mr. Reuterdahl's may lead to important conclusions.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 16, 1902, President Richards in the chair.

THE ELECTROLYTIC DISSOLUTION OF SOLUBLE METALLIC ANODES.

By Woolsey McA. Johnson.

The following theory of the electrolytic dissolution of soluble metallic anodes was developed by me some three years ago while a student in the laboratory of Prof. Nernst, of Göttingen. Later I used it to co-ordinate my ideas while conducting some experiments in the electrolytic refining of metals. As it proved useful to me in several ways I thought a short sketch of it might be of interest to the members of the Society. It contains nothing that should disconcert the most radical opponent of the dissociation theory, but, nevertheless, it is susceptible of expansion by means of this theory. To the best of my knowledge it has never been enunciated in any definite form before, although doubtless many people have arrived at similar conclusions.

To explain the facts which are known about the electrolytic dissolution of soluble anodes, we have recourse to the following known facts, *viz:*

1. Every metal has a certain specific electrolytic tension or voltage depending upon its temperature, physical condition and the solution in which it dips.

2. Every metal has a specific electrical conductivity.

3. These two properties are profoundly modified by alloying with other metals.

On these properties of the resulting alloys segregated in the anode, depends the selective electrochemical dissolution.

Metals unite with each other to form alloys, in most cases with the evolution of heat; in other words, the free energy is diminished, and as the electrolytic solution tension is measured by the free energy of the metal, in normal solution of its ions, it also must decrease; to express it in other words, the atoms are united with a firmer bond. The resultant product is harder and has less tendency to dissolve. Any carbides, sulphides, or silicides formed, are much harder to dissolve than the pure metal.

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The poor conductivity of alloys is well known. With the exception of several metals, as zinc and cadmium, etc., two metals unite to form an alloy having electrical conductivity below that of either, in many cases.

This second change caused by the formation of alloys in the anode is of greater importance than the first; for instance, we can consider a particle of silver-copper surrounded by pure copper crystals. In view of the great difference in electrical conductivity it is pretty certain that the current is shunted around this silver-copper alloy and finally dissolves its copper backing. It then can be brushed off into the "slime." This, of course, applies to all the alloys that have a low conductivity. For example, an alloy of 50 per cent. volume silver, 50 per cent. volume copper has a conductivity of 41.55 (Hg = 1). An alloy of 75 per cent. volume silver, 25 per cent. copper has a conductivity of 44.13. An alloy containing 0.9 per cent. volume tin and 99.1 silver has a conductivity of 20.08—about a third that of pure silver. These few examples show the tremendous effect of alloying, which by giving rise to counter thermo-electric forces reduces the conductivity out of all proportion to the amounts in which they are present. Usually the difference in electrolytic solution tension will cause unequal dissolution to a large extent. In the case of copper-silver, the values given by Wilsmore are copper —0.336 volt, silver —0.771 volt,[1] which show that the separation can be caused by a simple difference in the voltage. This we know by the cementing action of a silver salt by metallic copper.

$$Ag_2SO_4 + Cu = CuSO_4 + Ag_2.$$
$$Ag_2SO_4 + 2Cu = Cu_2SO_4 + Ag_2.$$

As it is known that the above reaction is almost quantitative, the constant of the reaction is large, consequently $ln\ K$ is also large. This can be also seen roughly by the difference in heats of formation with sulphuric acid.

An anode made by casting one-half part silver with 99½ parts of copper in such a manner that the amount of oxygen in the alloy as dissolved oxide is reduced to a minimum, can be electro dissolved in a solution containing Cu, 6 per cent., free sulphuric acid, 5 per cent., at a temperature of 45° C., and 90 to 99.9 per cent. of the silver will be "slimed," according to the current

[1] Ztschr. phys. Chem., 35, 3, 318.

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density. To be scientifically correct this current density should be measured in voltage (of which it is a function) against a standard electrode. If we make a "bi-metallic" anode, that is, a sheet of copper, by the side of which is a sheet of silver one two-hundredth of the size, it will be found that the silver goes in solution at a much lower current density than in the case of the alloyed anode. The only difference is that the silver is alloyed with the copper in the first case and not in the second.

The sliming of arsenic and antimony is another instance of the conditions favorable for copper electro-refining. Arsenic and antimony, were they present as metals, would have a greater tendency to dissolve than copper, because of their high electrolytic solution tension. The solution would require constant purification if pure cathode copper were desired. A very large percentage of these objectionable impurities can be slimed immediately. Th elarger portion of these elements are thoroughly oxidized in the converter or reverberatory furnace. The copper is then brought to "set" in the refining furnace and cast into anodes. The heats of oxidation of arsenic and antimony are six or seven times larger than that of copper. These oxides when once formed remain in the form of oxide dissolved in the copper and are not reduced to any extent in the "poling" operation while any cuprous oxide is left. These oxides are thus present in the anodes as insulators and as such pass into the slime directly from "oxidized" anodes.

These facts give to my mind a good explanation of the peculiar electrochemical behavior of the impurities present in anodes. The electrolytic refining of copper bullion has made it possible to produce very cheaply copper of high conductivity and save at the same time more than the assay value of the precious metals. With the possible exception of the "direct" steel process and the cyanide gold process it is the longest advanced step in metallurgy made in the latter part of the last century.

Accordingly it will seen that much is saved in copper refining by previous treatment of the anodes. A careful metallographical examination of the anode and some little thought on the alloys or compounds that can be formed, will reduce any electro-refining proposition to its simplest terms. What can be done may be tried, but it is well to know at times when we are "up against" the impossible.

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DISCUSSION.

DR. W. D. BANCROFT: Mr. President, I am sorry to call in question any of Mr. Johnson's facts, but the freezing-point curves for silver and copper do not show the existence of three compounds as I understood him to state. I know of two curves and no more, and what separates along one is not pure silver, but is silver containing up to 1 per cent. of copper, and, along the other, copper containing up to 1 per cent. of silver. That has been shown by the freezing-point curves and by microscopic examination. I think there is no evidence of the existence of three, or of any definite compounds between silver and copper.

DR. N. S. KEITH: I do not wish to discuss this paper; I wish to make an expression of dissatisfaction at the complications which chemists will put upon paper as existing in the refining of copper and separation of metals. I had in mind, and had hoped to bring before this meeting, a paper upon the subject of doing away with a great many of the complicated calculations which are put upon paper in regard to difficulties which seem to be more assumed than real.

It seems to me that the question comes back to "what are alloys?" Are alloys true chemical combinations, after definite rules and combinations, or are they mixtures? Are they solutions of one metal in another? Electrolytic refining of copper causes a residuum upon the surface of the anode of silver and other particles of metals. These particles have perceptible magnitude. Each one has weight; has size that we can measure without very delicate instruments. Now, can that anode be a true alloy or is it a mixture? If we are going to make theories based on the assumption that alloys are true chemical compounds rather than solutions of one metal in another, we had better settle the question first as to what are alloys. Having settled what are alloys, then we will have a basis upon which to found theories.

MR. W. MCA. JOHNSON: Mr. President, the experimental evidence on which the theory partly rests was found in refining other metals than copper.

In regard to what Professor Bancroft said in regard to there being but one minimum, if I made a mistake I am very sorry. I

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looked up those figures in Dammer's "Chemistry" and I thought I saw in the figures those minimas corresponding to simple formulas. If I made a mistake, or the determinations were wrong, nobody regrets it more than I do. It is, however, immaterial, as in any case the conductivity is lowered.

In regard to what Mr. Keith says about the secrets of copper-refining at the present day, I do not think there are any very great secrets in copper-refining. Everybody else that practices the electrolytic refining of copper is of the same opinion. If there are any secrets, they are purely in the details of the process.

As I said about the formation of silver sulphate and copper sulphate, it is only a rough qualitative test, because, as is well known, there comes in the right-hand side of the Gibbs-Helmholtz equation, which invalidates Thompson's rule. The only thing I can point out as new is the assembling of these several facts, which I have never seen anywhere else, and the fact that the high resistance of the copper-silver alloy or any other alloy is a great factor in the sliming of this alloy, and keeping the solution in a very pure condition.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 17, 1902, President Richards in the Chair.

STORAGE BATTERY INVENTION.

By Hugh Rodman.

Few problems are more attractive than that of improving the storage battery. The reward promised is enormous; the difficulty, apparently slight. We use lead to make a machine that should be light and strong. Why not substitute aluminum, zinc, iron, nickel, copper, in some suitable electrolyte?

Overcharge.—Besides charge and discharge, storage batteries must withstand overcharge, a putting in of more ampere hours than can be taken out. This is due partly to imperfect plates, an inability of the nearly-charged plate to change quickly, partly to local action, partly to individual differences among a number of cells in series that make it necessary to overcharge some cells in order to fully charge others. It is an action of the electrolyte alone. The plates serve only as indifferent electrodes between which the electrolyte is decomposed and the energy of the overcharge dissipated. The electrolyte must not change in character, but lose only its easily replaced solvent, water. In short, for the overcharge, we must have unchanging electrodes in an unchanging electrolyte.

Limits.—There are few such combinations. Organic electrolytes are in general changed. Chlorides oxidize and evolve chlorine. Bromides attack all common metals. Iodides deposit iodine. Borates, silicates and aluminates, with current of practicable density, deposit oxides. Sulphides and cyanides oxidize. Arsenates deposit arsenic. Manganates deposit dioxide. Nitrates attack all common metals, dissolving most of them. Phosphates dissolve all of them. Chromates dissolve all but aluminum and lead, in one case forming an insulating oxide, in the other a conducting peroxide. Sulphates dissolve all but lead. Hydroxides dissolve all but nickel. As lead in an alkali sulphate or chromate gives less than one volt pressure, the list of available anodes and electrolytes finally reduces to lead in sulphuric acid and nickel in an alkali hydroxide.

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This does not mean that the active material must necessarily contain nickel or lead, but simply that the grid, the current carrying part of the oxygen plate upon which the active material rests, must be one or the other of these metals in its appropriate solution. The active material of the oxygen plate, considering permanency only, may be any insoluble oxide or salt, while the grid and active material of the hydrogen plate, putting aside as impracticable any dissolving material such as zinc, may be either of the same metal as the oxygen plate, as lead in sulphuric acid, or else of some other metal soluble only at the end of a complete reversal of current, as iron in hydroxides. Practically, this all reduces to two classes: first, lead peroxide and spongy lead upon lead plates in sulphuric acid, the battery in general use, and second, mercuric or nickel peroxide upon nickel plates, together with cadmium, nickel or iron sponge upon iron or nickel plates in an alkali hydroxide, the battery proposed by Mr. Edison. As the most promising member of this latter type we may take an oxygen plate of nickel peroxide upon nickel with a hydrogen plate of iron sponge upon iron, and compare it with the usual Plante and Faure types of lead cell.

Grid.—The alkali battery possesses a great advantage in making its support plates of a stiff, easy-working metal. The stiffness insures absence of buckling (a trouble which must be considered and compensated for with lead plates), while the stiffness and ease of work together admit of a high mechanical perfection. It should be borne in mind, however, that the ordinary antimonial lead grid used with pasted lead plates is neither prohibitively heavy nor short-lived; it will probably last as long as the nickel grid when subjected to electrolytic action only; the inferiority lies in its mechanical weakness and in the difficulty of making fine castings.

Active Material.—Lead peroxide is a conductor. We can use it in comparatively large and porous masses. Nickel peroxide is not a conductor and so must be held in close contact with some conductor itself inactive, as nickel or carbon. This may be done in two ways: first, by peroxidizing a highly developed surface of nickel, corresponding with the Plante form of lead plate; second, by packing the active material or materials to become active with powdered or flake graphite, held rigid in a perforated box. An

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objection to the first method is, that as nickel peroxide does not conduct, only a thin layer of low capacity can be utilized; another objection is that the disintegration by shedding is even more pronounced than with lead and without the advantage of a continuing and compensating formation of the remaining metal. An objection to the second method is that the dense active mass impedes diffusion. An advantage is that the close held mass with its stiff finely perforated cover is apparently not subject to deterioration. It is well to note that the disintegration of one plate and long life of another is in no way due to the intrinsic qualities of one or the other active material, or to the difference in chemical action taking place; there is no apparent reason why lead peroxide reducing to lead oxide or to lead sulphate should fall to pieces any more quickly than nickel peroxide reducing to nickel oxide—in fact the reverse is true. The difference lies entirely in the method of holding the active material and in its porosity.

For hydrogen-carrying materials, we have spongy porous lead in the acid cell and in the other spongy iron or a low oxide of iron packed with flake graphite. Here we see no reason why the spongy lead plate should not last indefinitely, and, until recent years, this was supposed to be the case. It loses no material; it does not change chemically; but actually, its capacity lessens with age, and so, while its deterioration is not so rapid as that of the peroxide plate it must nevertheless be occasionally renewed. The opposite is now hoped for the iron plate; its active material is held rigid by a stiff grid and unchanging graphite packing and, apparently, should not lose capacity; this, however, for either iron or nickel can be proven only by a much longer life test than the plates have yet had.

Electrolyte.—One battery uses an acid solution that is absorbed during the discharge by the active material of both plates and released upon charge. The other uses a solution of potassium hydroxide that is inactive except as an electrolytic conductor, a means of carrying oxygen from one plate to the other. The result of this difference in electrolytes is most important; in the alkali battery we use only enough electrolyte to make a path for the current, while the acid battery must have a mass of electrolyte large enough to hold both the acid needed for the reactions and enough over to insure low electrolytic resistance at the end

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of discharge. Now, while the possibility of using a small amount of electrolyte, which means putting the plates close together, is one of the important factors in making the alkali battery light enough and small enough for commercial practice, this very advantage adds greatly to an already serious trouble—refilling. In overcharging, a portion of the water is uselessly decomposed, passes off as gas and must be replaced. The actual amount lost is fixed by the time of overcharge and by the current. The relative amount lost is inversely proportional to the volume of solution in the full cell. Here the alkali cell is inferior to the lead cell. First, the overcharge is greater. The densely-packed active material allows of only slow diffusion in its mass, with the result that a large proportion of the current breaks up the electrolyte at the surface of the nickel-plate, rather than pass through the attenuated alkali solution held in the active material and maintained there by the outward electrolytic movement of the potassium ions. Second, the current is greater. The voltage of the alkali cell is only about one-half that of the lead cell; therefore, for the same energy output, we must double either the current or the number of cells, so multiplying the useless dissociation by two. Third, the alkali cell has comparatively a small mass of electrolyte to draw upon. In all, the question of electrolyte mass comes to this: that, in the alkali battery we multiply a serious trouble by a factor of three or four and then halve the means of getting around it.

Another trouble arising from refilling is the quality of water used. In large commercial operation, or in laboratory work where distilled water can be gotten this is not serious, but with small users, where the hydrant is the common source of supply, it is often the means of putting into the electrolyte some active agent that eventually disintegrates the plates. Obviously, the lead battery has the advantage.

Again, the acid electrolyte is commercially the better for the ease of handling. This advantage will be overcome if the alkali battery will need no overhauling, but for the ordinary run of events, overturned cells, overfilled cells, handling of old plates, moisture from "gasing" in overcharge, for the numerous contingencies arising in actual work, there can be no question that alkali is worse than acid for wood-work, clothes and hands. Acid does not creep—alkali both creeps and turns to carbonate.

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The advantage sometimes claimed for the alkali simply upon the ground of its not changing is a little hard to understand. There is, on the face of it, no reason why the electrolyte should not change as well as the plates; in fact, a battery with unchanging electrodes and changing electrolyte would, in many ways, be better than its opposite. For instance, the change of electrolyte density is, in the lead cell, a very useful and needed means of determining the state of charge and discharge.

General.—Adaptability to different uses of one or the other battery will be finally determined by a balance between utility and cost. For central station work, which at present takes about 75 per cent. of the battery output, the position of the lead cell seems secure. Its low first cost, low internal resistance, high voltage and general efficiency more than overbalance the deterioration. This deterioration is a matter of careful figuring; in so many years so many plates must be manufactured and installed to keep a given battery in good condition; as an offset, so many pounds of scrap lead and so many pounds of battery mud are returned. The renewals ordinarily mean no interruption of work and not much expense in installing.

For lighter service, particularly for electric wagons, where watt-efficiency and cost are to some extent subordinate to convenience, the choice will depend largely upon capacity and reliability.

Data are wanting upon the capacity of the alkali cell per unit of volume and weight, but it seems reasonably certain that neither will be far different from that of the pasted lead battery. As for reliability, which must not be mistaken for long life, data on the alkali cell are again wanting and must be wanting until the cells are put into ordinary service with ordinary care and attention; it seems certain that the necessity for frequent refilling will mean serious trouble in the way of low cells and irregularity of working, while the problem of the alkali electrolyte and excessive "gasing" will need most careful consideration.

The commercial life of lead plates in truck or cab services is about 15,000 to 20,000 miles for negatives; 12,000 miles for Plante positives and 6,000 miles for pasted positives. In other words, a four or five-ton truck running 20 miles per day for 300 days in a year requires new positives once in a year or once in two years, according to the type of plate used, the choice of one

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or the other being determined by the character of service and length of run desired. Cabs and lighter wagons have about the same life with a capacity of 40 to 100 miles on one charge.

Work done under these conditions, actual work reduced to dollars and cents, has shown that the electric wagon gives better city service than can be gotten from gas, or steam, or horse. A better battery, either an improvement on the old or a better new one, would control practically all city traffic not on rails.

DISCUSSION.

DR. N. S. KEITH: Mr. President, I think Mr. Edison provides against creeping and carbonation of a solution, by covering it with petroleum.

MR. C. J. REED: I believe that according to report Mr. Edison has succeeded in operating a carriage with a very light battery of this type, weighing only about one-half what the usual lead battery weighs, and making about twice the distance under more adverse conditions, and up grades about twice as steep. I say this from reports that have been published. I do not know anything about it personally. If these reports are true it would seem that all these difficulties had been overcome.

DR. KEITH: I may add to Mr. Reed's remarks that many of these difficulties are more theoretical than real. I know something analogous. It was argued against the cyanide treatment of ores for the extraction of gold, that the presence of carbonic acid in the atmosphere would so deteriorate the solution of cyanide of potassium, converting it into carbonate of potassium, that it would be practically impossible on account of cost to continue the process; but in practice it is found that this possible result is a negligible quantity, amounting to a half cent or a quarter of a cent to a ton of ore treated. It may be that the carbonation of the caustic alkali solution is not a very serious objection.

MR. DODGE: I would like to state in regard to that carbonating that, as a matter of fact, it is a very practical and serious difficulty. I have done considerable experimenting on that line, and cells, if allowed to stand at all, take up carbonate very readily. I understand that it is guarded against to a very considerable extent by the cells being covered with a rubber cover, with a pin-hole through the top to allow the escape of gases.

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MR. A. LARCHAR: It may be pertinent to note, in addition to what Dr. Keith has said, that in certain decomposing cells where the cathode solution is alkaline and the escaping gas hydrogen, carbonating is prevented by the use of a film of heavy hydrocarbon oil. I have used this in experimental work and found it very effective.

DR. KEITH: It is used in the Edison battery for that purpose.

MR. H. RODMAN: In regard to the carbonating, it is not so much the question of cost as the question of the effect on the battery. The effect is considerable, as the battery not only loses in voltage but loses in capacity. In regard to covering with hydrocarbon, I do not think it is possible in actual service.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 17, 1902, President Richards in the Chair.

SOME ADVANCES IN THE CLOSED AND CONTINUOUS WORKING ELECTRIC FURNACE.

By Edward R. Taylor.

In continuity, for most chemical manufactures, there is great gain, and for some it is almost an absolute necessity. Movable electrodes in a closed electric furnace present serious difficulties, such that continuity of operation with them is practically impossible; the continual wearing out of their terminal ends must be provided for in some other way and their replacement in some manner becomes a necessity.

In such a furnace, if continuous work is to be done, an electrode moving through a stuffing box (for the manufacture of such a body as bisulphide of carbon, for example) is practically out of the question. The use of pieces of conductive material that can settle down upon each other from above and properly arrange themselves and feed down by gravity, early commended itself to my thought; but a suitable and proper arrangement to meet all the required conditions did not immediately appear. A conduit of sufficient surface to conduct large amounts of current to such broken material, without offering such resistance as to determine the conversion of large portions of electricity into heat before reaching the active part of the furnace, would afford also a large surface for insulation against the passage of electricity into the shell of the furnace. I therefore reached the solution of the difficulty by a compound method, *i. e.*, by carrying the current into the furnace by the use of a stationary conductor of moderate size, and separately arranging the moving portions inside of the furnace itself.

Noticing the construction illustrated in connection with the paper that I had the honor to read before this body at the Philadelphia meeting,[1] it will be seen that there is presented a plan of

[1] These Transactions, Vol. I, p 115.

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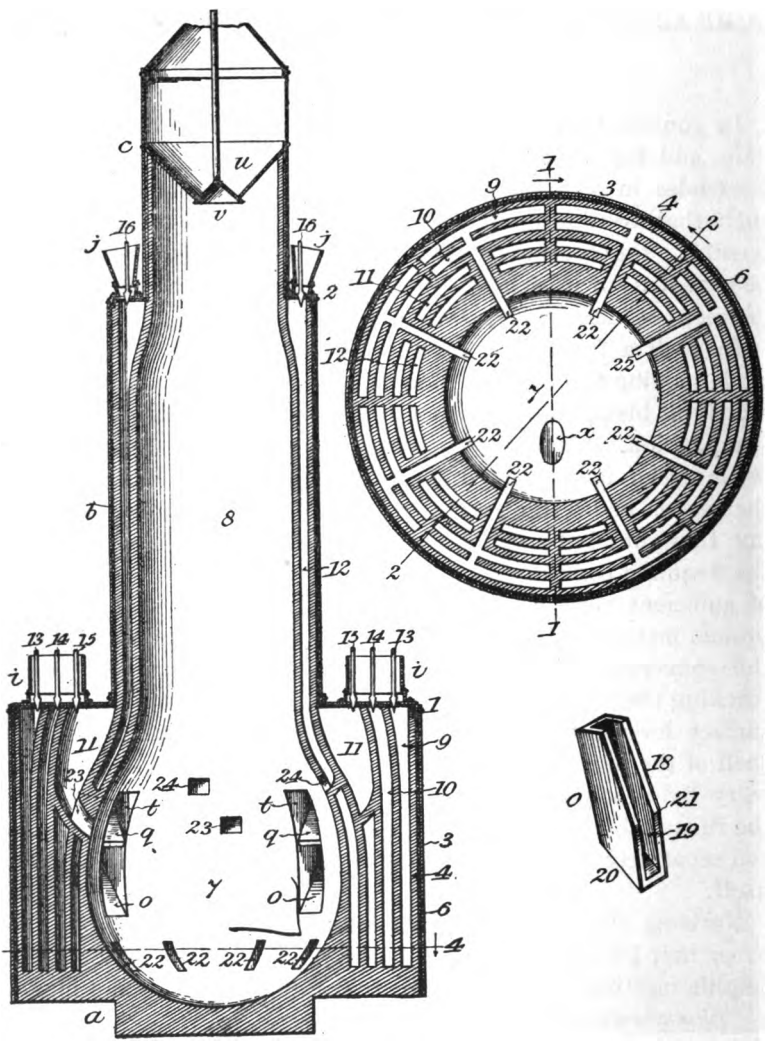
prolonging the life of the electrodes by regularly feeding upon them and at their ends, by gravity, broken conductive material; whereas in the plan illustrated by this paper we may properly leave out the word prolonging and say that we have for all practical purposes made a live electrode; or in other words we have a self-renewing electrode in a closed furnace—a continuously reproducing electrode, the broken and moving portions of which



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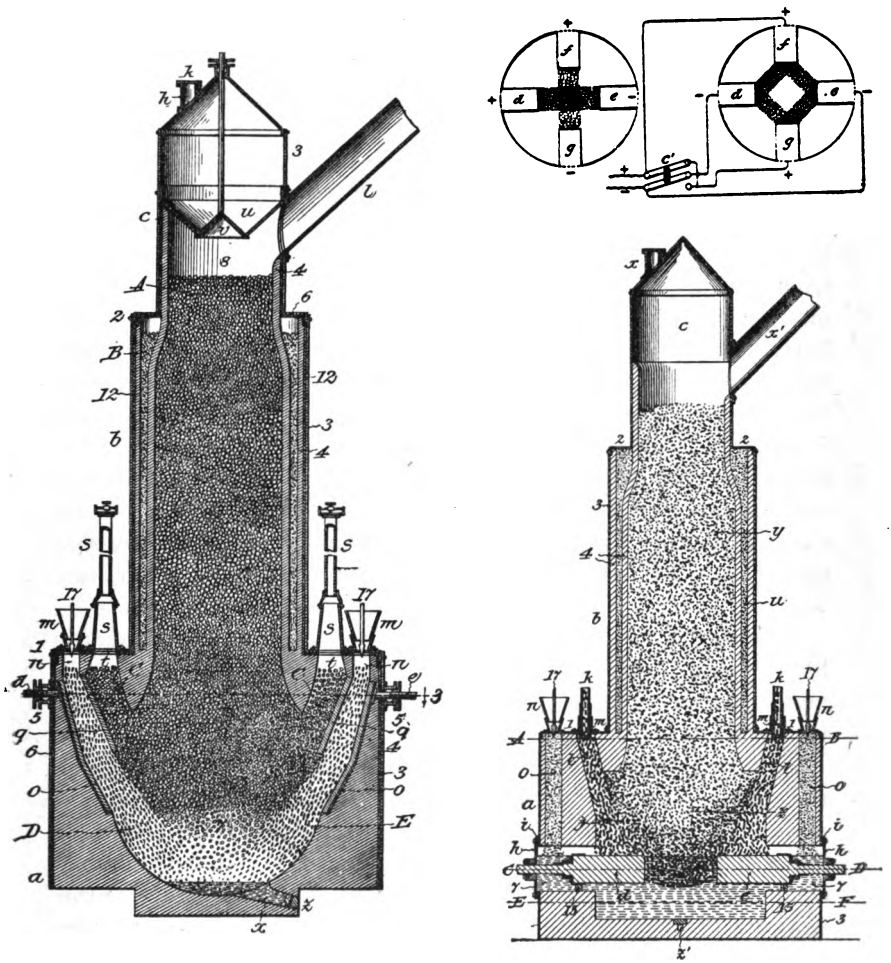

in their continual descent, themselves constitute the electrodes.

New material constantly descends and takes the place of that exhausted at the ends or points of wear.

The conduits through which these broken pieces are fed are suitably connected by an insulated conductor, through the shell of the furnace, to the source of electricity. Suitable hoppers are made above the conduits and outside of the furnace through which the broken conductive material can be fed into and ultimately through

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the several conduits, at the bottom of which the broken fragments are free to arrange themselves by gravity so that the weakest part of the circuit will be determined where the pieces come together at the bottom of the furnace. As fast as the lower ones are exhausted others feed down from above and take their place, and thus the continuity of the electrodes is maintained.

A second requisite for an electric furnace that shall be capable of continuous and prolonged use, without stopping to clean out, is that either a non-volatile product or residue may be removed from the furnace either continuously or at intervals in a fused or molten state. This provision is clearly shown in the illustration before us. Our honored president was kind enough to say that my present furnace "is a revelation of what may be expected in the size of electric furnaces in the future." In this connection I will say that with this construction of the furnace and an adequate source of electricity at my command, it would take less nerve on my part, with my present experience, to construct an electric furnace that would dwarf the largest blast-furnaces in existence to-day, than it took to build the furnaces now in use, which are 16 feet in diameter and 41 feet high.

To prevent the passage of electricity through the furnace at a higher level than desired, a wall made of suitable non-conductive material constitutes the front side of the conduits which is shown in the illustration.

Provision is also made to increase or reduce the resistance of the furnace at will by feeding conductive or non-conductive material through openings provided in front of the conduits, down upon the working ends of the electrodes. In this manner comparatively quick changes can be made in the resistance of the working furnace, permitting its increase or diminution as may be required for the best results in utilizing the current and the best production of goods.

If at any time piers should form in the furnace tending to hold up the charge, they can easily be reduced by changing the path of the electricity through the furnace from opposite to adjacent pairs of carbons. This feature is shown in the illustration. There is therefore nothing that can interfere with the regular descent of the furnace charge and the regular continuity of the work.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 17, 1902, President Richards in the Chair.

THE PHENOMENON OF THE FORMATION OF METALLIC DUST FROM CATHODES.

By PROF. DR. F. HABER, of Karlsruhe, Germany.

Mr. President and Gentlemen: I take great pleasure to tell you first, that the "Deutsche Bunsen Gesellschaft für Angewandte Physikalische Chemie," better known perhaps to you under its former name, "Deutsche Electrochemische Gesellschaft," was delighted to notice that an "American Electrochemical Society" was inaugurated. I believe it is very important that a Society should form the common ground for the electrochemical interests in the United States, where, favored by natural resources and fostered by broad-minded and indefatigable chemists, a wonderful development of electrochemistry has been accomplished. I want to express the heartiest wishes for the further success of your work, as well in the name of the German sister Society as in my own name. Further, to contribute a little to the success of your meeting, I venture to bring before you, in a condensed form, some results which I obtained during the last few years in co-operation with my friend, Prof. Dr. Bredig[1], at Heidelberg, and also with one of my pupils, Mr. Sack[2], who will publish our investigation in full in the *Zeitschrift für anorganische Chemie.*

The phenomenon I am about to speak of is a very astonishing one and there are so many chances to observe it, that certainly many of you have witnessed some of the facts which I intend to explain. Indeed, nobody who occasionally uses a cathode of lead in a solution of caustic alkali will fail to wonder that by increasing the current density, suddenly black clouds will form on the cathode. The clouds fill the electrolyte and color it like ink. A few days ago your distinguished secretary, Mr. C. J. Reed, kindly gave me a paper read by him some years ago,[3] which I

[1] Bredig and Haber: Ber. d. deutsch. Chem. Gesellschaft **31**, 2741 (1898).

[2] Haber and Sack: Ztschr. Elektrochem. (1902), **8**, and Haber: *Ibid.*, (1902) **8**.

[3] C. J. Reed: Jour. of the Franklin Inst., April, 1895.

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did not know before, describing this very phenomenon and expressing the idea that unknown products form on such a cathode.

We have observed the same phenomenon in using cathodes of tin, bismuth, thallium, arsenic, antimony and also mercury. I do not wish to take up too much of your time, and think it will be sufficient if I show here the effect with a cathode of tin and a cathode of lead. I add that the phenomenon is not confined to a solution of caustic alkali, but that every salt of potassium or sodium gives the same result if there are no deposits of a foreign body on the cathode. These facts, first related by Mr. Bredig and myself, seem to contradict every electrolytic experience. As a rule anodes are affected, but cathodes are regarded as perfectly stable during the passing of the current. Nor seem at first our observations explicable from a theoretical point of view. If the current passes from the alkaline solution into the cathode, etc., H-ions, or the ions of the alkali metal may be discharged. The H-ion would give directly hydrogen gas, the discharged alkali-ions would react with water, developing hydrogen secondarily. It has been frequently discussed whether the development of hydrogen on cathodes in alkaline solutions is produced directly or secondarily. But no chemical fact was known which settled the matter definitely.

Investigating this matter more deeply, it is evident that there is a third possibility which formerly escaped attention.

If the alkaline metal is deposited on the cathode, may we not expect that it would combine with the metal of the cathode, provided that such a reaction would be an easy one? Might there not be formed alloys between the discharged ions of sodium or potassium and the lead or tin, if sodium and potassium are able to combine with lead and tin? And if there would be formed such an alloy, may we not expect that on the surface of the cathodes the same reactions would take place which are observed when these alloys, prepared in the usual chemical way, come in contact with water? And now let us ask, what chemical properties the alloys of sodium and lead or sodium and tin possess? The metals, lead and tin, are practically not reacted upon by cold solutions of caustic alkali. If we make an alloy containing only a small percentage of alkali metal, a continuous quiet current of hydrogen is produced on contact with water. But if we prepare an alloy rich in alkali metal, we find that on contact with alka-

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line solutions or water, exactly the same clouds of metallic dust are formed which we observe on cathodes of lead, tin, and the other metals mentioned before. It is due to the rapid decomposition of the alloy and to the stormy generation of hydrogen that these clouds of metallic dust are carried off. The phenomenon of the formation of metallic dust from cathodes is, therefore, explained by the simple fact that the cathodic metals form alloys with the discharged alkali ions, and that these alloys act on water in this peculiar manner. In explaining the phenomenon, this fact proves at the same time conclusively that alkaline ions are discharged.

We thus see that the formation of metallic dust is due to alloys rich in sodium or potassium. The question is, now, whether alloys with a small percentage of alkali metal could be formed on cathodes, and if such are formed what changes would they produce on the surface of the cathode. Considering that rich alloys cannot be formed without an intense discharge of cathions, we may expect that poorer alloys will be formed if the density of the current is a smaller one. Now let us carefully investigate what change takes place if the current is not strong enough to produce these clouds of metallic dust. If an alloy is formed and afterwards decomposed by the action of water, the smooth surface of the lead or tin cathode will become rough, its metallic luster will be spoiled and it will look somewhat spongy. Indeed this is really observed. Any current not as dense as to produce metallic dust will effect this result with lead and tin. The metals which are affected by the current so that cathodes made of them become rough and spongy under the above conditions are much more numerous than those which form metallic dust. The reason for this fact is that the most metals do not easily form such alloys with alkali metal which are decomposed by water under the formation of metallic dust. A type of the former class of metals is zinc, which becomes rough but never forms metallic dust if used as cathode.

Having proved by my experiments these changes on cathodes in alkali solutions, it may be asked what takes place in acid solutions. It is of no interest to discuss neutral solutions because no solution remains neutral on the cathode if hydrogen is generated.

Formation of metallic dust was also found in acid solutions,

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using lead and bismuth as cathodes, but this formation is much more difficult to produce and not so striking as in alkaline solutions. I believe that an alloy of hydrogen with these metals is formed which is rapidly decomposed, evolving hydrogen on contact with water. It is a remarkable fact that bismuth and lead stand at the end of such groups in the Mendelejeff series, which form combinations with hydrogen or with alkyl. Bismuth stands on the end of the phosphorus-arsenic-antimony group, whereas phosphorus and arsenic form rather stable hydrogen compounds; antimony forms a compound which is already decomposed on standing in watery solutions. The stability of this hydrogen compound decreases with increasing molecular weight and, therefore, the formation of metallic dust in the case of bismuth may be justly explained by assuming that the formed bismuth hydrogen compound possesses the property of decomposing at the moment of its formation. The same is the case with lead, which ends the group silicium, germanium, tin, and lead, which all form stable alkyl compounds, while only the first two form stable hydrogen compounds.

But if the formation of metallic dust is more difficult to produce in acid solutions, the other phenomenon of disgregation can be very easily seen. I mention only that in acid solutions a platinum cathode at a high current density becomes perfectly black and spongy, as if it were thickly coated with platinum powder, while in alkaline solutions never more than a slightly roughened surface will be observed.

This fact is in conformity with what we may expect. The hydrogen, if formed by the discharge of the H-ions, enters much more easily into the deeper sheets of the cathodic metal than the sodium and potassium, which are of higher atomic volume and less mobility. This explains the differences in the behavior of platinum in acid and in alkaline solutions.

Let me add that in all these experiments no sparking or formation of electric arc interferes. Distilling of metals or other thermic action is therefore to be excluded. I insist upon this point because, in cases of very high current density, pure thermic action upon cathodes which destroys them it is neither new nor astonishing. There is no connection between this thermic phenomenon and the peculiar facts to speak of.

Mr. President and Gentlemen: The subject seems perhaps to

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be of more theoretical than practical interest. But because it may happen that these phenomena are observed and cause astonishment and surprise in pure practical work, I hope you will regard it worth while to be mentioned at this place, at the central point of the electrochemical industries of the world.

DISCUSSION.

DR. N. S. KEITH: Mr. President, I desire to ask Professor Haber if the dust thrown off has been tested for its quality as an alloy or possible alloy; as, for instance, potassium and lead or potassium and tin. If alloys are thrown off it would seem to me that in the solutions they would be subject to oxidation, potassium or sodium would be set free and oxidized, and possibly there might be the formation of plumbate or stannate of potassium or sodium, as the case might be. This is certainly a very interesting experiment, and the professor's explanation seems to me the correct one.

DR. W. D. BANCROFT: I should like to ask Dr. Haber also whether there is possible any connection between this tendency to form a cathodic dust in solution when there is simply alkali or acid present, and the fact that certain cathodes have a much greater reducing power than certain others. As instances of this there are the experiments made by Tafel who found that certain of the alkaloids could be reduced with lead cathodes, whereas they could not when other cathodes were used. Analogous experiments have been made on the reduction of potassium chlorate. Of course, the theory which simply assumes that hydrogen is set free does not explain in any way the experimental differences which we find in the cathodes, whereas it seems quite possible that there might be some connection between this formation of alloy and tendency to disintegration and the reducing power of those cathodes.

PROFESSOR F. HABER: Mr. President, I am in perfect agreement with Mr. Keith that the alloy if it comes in contact with water, is decomposed. But it was my intention to say that the dust is of lead and tin and not of the alloys. Alloy is formed on certain of the cathodes, but directly after it has been formed it decomposes, and the dust is that of the more stable or insoluble metal.

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In regard to the other question of Mr. Bancroft, I agree with him, and I believe it is of much importance for the reduction of some materials at the cathodes, that such alloys form. But it is difficult to say exactly what is the connection between the formation of alloy and the degree of conductive power, and I am unable to give elaborate details in this connection. I hope, by going further in investigating reduction reactions, we will find the connections in this direction which Mr. Bancroft suggested.

MR. C. J. REED: Dr. Haber has kindly referred to the paper which I read at the Franklin Institute some years ago (Feb., 1895), in which I described and exhibited the same phenomenon with lead cathodes. I did not make extensive investigation of other metals, and in those experiments I succeeded in pulverizing the cathode only with lead and arsenic. In the case of lead I found that borax solution gave the most voluminous clouds and I noted at that time that, by bringing the lead cathode close to the edge of the beaker and examining it very closely, a bright reddish stream of what appeared to be a powder came off directly from the lead cathode. Before this powder proceeded more than one-eighth of an inch from the cathode it changed into lead powder. A chemical examination of the powder showed that it consisted of nothing but lead. I was induced to conjecture from the appearance of the reddish stratum that the actual cause of the phenomenon was the formation of some compound of lead with some ion of the electrolyte; but I did not conjecture that it was the alkali metal. My conjecture was that it was a compound of hydrogen and lead, but I think the experiments with lead alloys, which Dr. Haber has referred to here, show that it is probably due to the formation of an alloy of lead with the alkali metal.

DR. H. S. CARHART: I have a small contribution to make relative to the alloying of the cathode, an observation which I made several years ago. I think it has been published, but it comes in beautifully in this connection. I was decomposing zinc sulphate with a very small current, with platinum electrodes and one-tenth of an ampere only, I think, and perhaps nearly fifty square centimeters of surface of platinum, the operation continuing for five or six hours. At the end of the time I opened the circuit and left the apparatus standing. In a few hours the platinum plate became very black. The fact was that the zinc

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had alloyed with the platinum as it was very slowly electrolyzed, and upon standing in the solution there was free acid enough to remove the zinc and leave a very finely divided platinum. If you want platinum black that you cannot get off, this is the best way to get it. You can not get it all off by scraping. It is part of the platinum surface.

PROF. HABER: This is a very important observation by Dr. Carhart, and I wish to add that the phenomenon pointed out by him will occur very easily if you attempt the determination in an electrolytic way in a platinum bowl, following the method of Classen. Then you have always a deterioration of the bowl because this very phenomenon which Dr. Carhart speaks of occurs. Therefore, it is one of the first things that is taken into account in analytical electrochemistry, to make an allowance in making determinations for the loss of weight of the platinum bowl, because the platinum bowls become deteriorated; but I believe this is a later experiment, and Dr. Carhart was the first to point out the phenomenon.

DR. LOUIS KAHLENBERG: In all plating processes this question of alloying becomes important. This is an especially striking instance of it, to be sure. We all know that we cannot successfully plate nickel on iron. The deposit will not adhere well. We first plate copper on the iron, and then we plate the nickel on the copper. Why do we do this? Does any one suppose that an electroplated metallic coating sticks on the metal underneath simply by adhesion? No; it is the alloying process that determines the strength with which that coating adheres. And here we have simply a very striking illustration of that fact. So it seems to me this is only a special example of a general, very fundamental proposition of electrochemistry.

MR. REED: I would like to mention one other fact in confirmation of that statement. It is in case of electrodeposition of zinc from zinc chloride upon copper at a temperatue a little above one hundred centigrade. If we use a strong solution of zinc chloride, the zinc immediately alloys with the copper and produces a bright yellow surface of brass which unquestionably proves that the alloying has actually taken place.

DR. BANCROFT: Some years ago Dr. Kahlenberg described

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the electrolysis of lithium chloride in pyridine solution. He there used an iron cathode. He said, also, we could use a platinum cathode. We repeated the experiment last year, as a lecture experiment, and we found to our great surprise that while you can get lithium precipitated without any difficulty at all on the iron, if you use platinum it is very difficult indeed to get any lithium precipitate. We did not carry it further. Dr. Kahlenberg tells me he has the same difficulty, but by carefully carrying out the conditions you can get the lithium precipitate on the platinum.

MR. TAGGART: Professor Haber referred to the deterioration of platinum vessels used for the determination of zinc electrolytically. It is customary to first deposit silver or copper on the platinum and then the zinc, in order to insure the complete removal of the zinc from the platinum.

DR. KEITH: There is no trouble whatever in removing the deposit by a solvent. In removing copper from a platinum cathode in analytical work, the surface of the platinum does not seem to deteriorate. It turns out as bright after the copper is removed as before. After using a cathode a great many times in that way, I have not found any variation in the weight, or any deterioration of its surface.

PROF. HABER: I think in this case the effect is not a visible one.

PRESIDENT RICHARDS: I think that I have observed the formation of similar metallic dust in experiments for purifying aluminum electrolytically in aqueous solution, and using a solution of alum which contained the alkaline metal. On passing the current there is an exceedingly dark cloud of apparently metallic dust formed around the receiving pole, the cathode. It is particularly noticeable in attempting to deposit the aluminum, and it may have been caused by the union of the alkaline metal there with the aluminum cathode on which I was trying to deposit from an aluminum anode. I may say that the experiments did not succeed. I succeeded only in plating a very small amount of aluminum, most of it coming down as hydrate. But the solutions became black very quickly from the formation of this metallic dust.

If there is no further discussion I will extend to Professor Haber the thanks of the Society for his paper and for the greeting he has brought to us from our sister Society. (Applause.)

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 17, 1902, President Richards in the Chair.

THE THEORY AND PRACTICE OF CONTINUOUS-FLOW ELECTRIC CALORIMETRY.

By H. T. Barnes, D.Sc.

The method of continuous-flow calorimetry may now be said to be fairly well established. The announcement of the method was made by Professor Callendar and the author, at the meeting of the British Association at Toronto, in 1897. Since then various papers have appeared from time to time describing the experiments carried out by the method.[1] The scope of the present paper is to set forth, in as simple a manner as possible, the general theory, in the hope that it may prove to be of some practical value to those who desire to undertake actual calorimetric measurements by the method. Since the other papers, giving all the details of the theory and practice of continuous calorimetry may be obtained, it is not necessary to give more than a brief account here. The writer desires, however, to point out how simple the method may really be made, and to suggest a simple form of calorimeter for laboratory use.

If we have a flow of liquid Q per second, continuously heated by an electric current in a fine flow-tube enclosed in a vacuum jacket, the walls of which are maintained at the temperature of the liquid flowing through, then

$$Js\mathrm{Q}\partial\mathrm{T} + \mathrm{H} = \mathrm{EC},$$

where J is the number of joules per calorie.

s is the specific heat of the liquid.

∂T is the difference of temperature between inflow and outflow.

H is the heat loss.

EC is the electrical energy supplied per second.

Writing an approximate value for s, *i. e.*, s_0 then $Js_0(\mathrm{I} \pm d) = Js$, and dividing by ∂T we have

$$Js_0\mathrm{Q}d + h = (\mathrm{EC} - Js_0\mathrm{Q}\partial\mathrm{T})/\partial\mathrm{T},$$

[1] *Phil. Trans.*, A, Vol. 199 (1902).

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which may be called the general differential equation of the method.

In all methods of calorimetry, the heat loss is by far the most uncertain correction to determine. By the method of continuous calorimetry this correction, owing to the use of a vacuum-jacket, is reduced to that of radiation from the heated walls of the flow tube to the walls of the vacuum-jacket. The conduction error, the writer has shown elsewhere, is negligibly small above certain limits of flow, while errors due to convection are obviated by devices for promoting the adequate stirring of the flowing liquid.

The value of h depends on T only, and is, therefore, independent of Q. By taking two values of Q the value of d may be calculated by combining two of the general difference equations and eliminating h. Since h is different for different temperatures, the experimental arrangements must be such as to give the same mean temperature between inflow and outflow.

In the long series of experiments which the writer has carried out in his laboratory at McGill University, to determine the variation of the specific heat of water and mercury with temperature, various devices have been employed to reduce the error of experimental reading, and to render the measurements independent of surrounding influences. These may be summarized briefly as follows: an accurate potentiometer for determining the fall of electrical potential across the heating wire placed through the flow tube and that across a standardized resistance, for determining the current, in series with the heating wire; carefully constructed Clark and Weston cells; electrical thermometers for measuring the inflow and outflow temperatures; a sensitive thermostat for maintaining the temperature constant at different temperatures between 0° and 100° C.; a standardized clock with recording chronograph and a set of standard weights. In employing the method for measuring specific heats and as a laboratory instrument for demonstrating the method of measuring the specific heat of water, much simpler arrangements may be adopted. For an order of accuracy of one or two parts in a thousand, Weston electrical instruments may be used, and mercury thermometers substituted for the platinum. This simplifies the labor of the observer very much, and at the same time gives excellent results. The accuracy and reliability of the Weston instruments makes the measurement of the electrical energy comparatively simple.

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As an example of the method of calculation for the vacuum-jacketed calorimeter we will cite two sets of results taken from the writer's experiments. The first is for water in which case the value of s is very nearly equal to one at any part of the scale. The following is taken from the writer's paper, p. 243, (l. c.):

$$\left.\begin{aligned} EC &= 20.8711 \text{ watts} \\ 4.2Q\partial T &= 20.5765 \text{ watts} \end{aligned}\right\} Q = 0.572619 \text{ gram per sec.}$$

and

$$\left.\begin{aligned} EC &= 13.7319 \text{ watts} \\ 4.2Q\partial T &= 13.4213 \text{ watts} \end{aligned}\right\} Q = 0.372504 \text{ gram per sec.}$$

The approximate value of Js_0 is here taken as 4.2 joules.

Substituting in the general difference equation we have:

$$2.405d + h = 0.03446$$
$$1.564d + h = 0.03621$$

from which by eliminating h, $d = -\frac{0.00175}{0.841} = -0.00208$.

Hence $Js = 4.2(1 - 0.00208) = 4.1913$ joules, or taking the value of the thermal unit at 15.5° C., which is equal to 4.1891 joules, s is found to be equal to 1.0005.

A similar example for the mercury calorimeter when the value 0.140 is substituted for Js (*i. e.*, 4.2×0.0333) gives $d = -0.00584$, which gives for Js the value $0.140(1 - 0.00584)$ or 0.139182, or for s the value 0.033224.

It must be pointed out that the above method of calculation depends on the heat loss being that of radiation only, which only holds for the vacuum-jacketed calorimeter. Experimental tests may be applied to check this. It will be seen that such an uncertain correction as the heat capacity of the calorimeter does not enter into the calculation on account of the steady temperature conditions.

SIMPLE FORM OF CALORIMETER.

The writer has been experimenting recently on a simple form of continuous-flow calorimeter. The great disadvantage of this for actual determinations is the quantity of liquid required. From one to two liters will be wanted for convenience in working, which in many cases would be quite impossible to obtain. As an instrument for showing to students the relation between the electrical and thermal units, and determining the specific heat of water, it has such great advantages over the older methods of calorimetry that it seems desirable to describe it here.

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Two classes of liquids have to be considered ; conductors of electricity in which case electrolysis results, and non-conductors. For the latter the electric heating wire may be placed directly in the liquid ; for the former an insulated heating wire is required. The use or not of a vacuum-jacket will depend on whether absolute or only relative measurements are required. In the former case the method of treatment may be adopted as just described (supra), but for the latter an initial experiment with a liquid whose thermal capacity is known determines the value of the heat loss for each particular calorimeter. A calorimeter without vacuum-jacket must be wrapped in flannel, or other lagging material, to reduce the heat loss, but the method of treatment of the equations for eliminating the heat loss no longer holds.

The heating wire is wound in a spiral, and so placed in the flow tube as to mix the water as much as possible. The heating current is led to the wire by means of small copper tubes which have been carefully covered with tin. Through the center of the tubes potential leads are taken to the heating wire and the whole soldered with pure tin solder. The potential wire is insulated from the tube through which it passes and, coming out of the calorimeter as it does, the ends of the calorimeter may be closed by a metal or rubber stopper through which the copper tube passes. Thermometers are placed in the inflow and in the outflow tubes by means of suitable glass T-joints. As the success of the experiments depends on the attainment of steady conditions care must be taken to arrange the experimental conditions with this end in view.

The liquid must be supplied from a constant level head, which is made most conveniently from a simple overflow device placed near the calorimeter and elevated sufficiently to give the desired head. The overflow device is supplied from a second reservoir, which is replenished repeatedly by hand from the outflowing liquid. In the case of water the overflow device may be supplied directly from the water mains. To maintain a constant temperature of inflow, where a liquid other than water is used, it is necessary to pass the liquid through a cooler first before it enters the apparatus.

As an instrument for student use to show the relation between the electrical and thermal units the experiments may be carried out very quickly and easily. A preliminary experiment by the

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instructor determines once for all the value of the heat loss to be used by the student as a correction factor in the calculations.

As an illustration of experiments by the simple calorimeter the writer cites the following which were carried out with no pretence at great accuracy. The calorimeter was supplied with a heating wire of 10 ohms resistance wound in a spiral and nearly filling the flow tube, 5 mm. in diameter. Two Geissler mercury thermometers, reading to $^1/_{100}$ of a degree, were placed in the inflow and outflow. The water was supplied to the constant level overflow device directly from the college mains. This overflow could be raised and lowered at will so as to change the head. For heating current the 100-volt experimental circuit was available with an external adjustable rheostat. A Weston millivoltmeter with a 10-ampere shunt was used for measuring the current. This instrument was calibrated carefully in terms of standard electrical instruments. A Weston 100-range voltmeter, for which a calibration curve had been obtained, served to give the drop of potential across the heating wire. The resistance of the heating wire was selected with reference to the electrical supply. Had it been necessary to use smaller values of E and larger values of C, as would be the case when a battery of accumulators is used, it would have been necessary to have the heating wire of smaller resistance. This is, however, a matter of selection on the part of the observer. In the present case 10 ohms were found very satisfactory. In fact the full 100 volts could be turned on without the least damage provided the flow was at the same time increased to compensate for the excessive rise of temperature produced..

The method of measuring the product EC instead of C^2R is always to be preferred since the result is independent of the superheating of the wire which always takes place in electrical calorimetry. The flow was measured by introducing a weighed flask quickly under the stream of outflowing liquid, and at the same time a stop-watch started. At the end of two or three minutes, after a sufficient quantity of liquid had been collected, the flask was removed and the total time obtained on the stop-watch. The following table contains the result of the measurements with different flows and different rises of temperature :

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TABLE OF OBSERVATIONS.

Q.	∂T.	4.189 Q∂T.	EC.	Diff.	Heat loss in per cent. of supply.
4.913	6.01	123.7	126.3	2.6	2.11
5.120	22.79	488.9	500.4	11.5	2.35
6.938	11.73	339.5	347.9	8.4	2.48
6.934	11.73	339.3	347.9	8.6	2.54
4.375	11.66	213.7	218.7	5.0	2.34
4.344	11.77	214.2	218.7	4.5	2.10
2.702	11.68	132.2	134.9	2.7	2.05
2.677	11.76	131.9	134.9	3.0	2.27

The heat loss remains a constant percentage correction of the total heat supply, as will be seen by reference to the last column in the table. A second series of results similar to these were obtained for a calorimeter with a flow tube more than twice as large as the present one, but although the heat loss was greater the final result was the same and showed the same relationship between the loss and the total supply. This simple relation simplifies the measurements very much since, within wide limits, all flows and all rises of temperature require but the same correction factor to compensate for the heat loss. This correction factor becomes then a constant for the calorimeter, one careful experiment being sufficient to determine it for each particular calorimeter.

A DETERMINATION OF THE SPECIFIC HEAT OF WOOD ALCOHOL.

As a test experiment the ordinary commercial wood alcohol was employed in the apparatus. The following table gives a summary of the observations:

TABLE OF OBSERVATIONS FOR WOOD ALCOHOL.

Q.	∂T.	4.189 Q∂T.	EC.	s.
1.619	8.46	57.38	37.84	0.644
1.798	7.33	55.44	36.20	0.640
1.619	8.44	57.27	37.76	0.644

Under Q is given the flow of liquid in grams per second. ∂T contains the rise of temperature. The third column contains the product JQ∂T, while the fourth column gives the value of EC. Adding 2.3 per cent. correction to the product in the third column, to allow for the heat loss, the value of *s*, the specific heat of the alcohol, is obtained. Values previously obtained for ordinary alcohol, which differs but little from wood alcohol, vary from 0.615 (Kopp) to 0.659 (Reis). When the wood alcohol

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was diluted with 50 per cent. of water the specific heat was found to have increased almost to unity. Two measurements with the continuous-flow calorimeter gave 0.973 and 0.970.

It will be seen that the method is applicable for measurements of specific heat to a fair order of accuracy with the simplest form of apparatus. The ultimate accuracy merely depends on the observer and the refinement to which he wishes to carry the measurements. It must be claimed for the method of continuous-flow electric calorimetry that, owing to the production of perfectly steady temperature conditions, experiments may be carried out with more accuracy than with the older methods, with the expenditure of much less time and energy in the arrangement of the apparatus and in observation.

Messrs. Eimer and Amend, of New York, constructed and exhausted for me four vacuum-jacketed calorimeters from designs which I used throughout in my investigations on the variation of the specific heat of water and mercury. They no doubt would be willing to undertake the construction of the simpler form of calorimeter with the same efficiency.

FURTHER APPLICATIONS OF THE METHOD.

The principle of the method may be applied in a number of ways. As a comparative method for specific heats, a continuous method of mixture may be arranged in which a steady stream of the liquid under test is mixed with a steady stream of water at a different temperature. In this case no electrical measurements are necessary, the heat supply being calculated from our knowledge of the thermal capacity of water. When heat is developed in the mixture of the two liquids this may be determined beforehand and corrected for.

The method may also be used to measure the heats of dilution. These methods are now under test by the writer, so that nothing definite can be said at present in regard to the practical working. This, it is hoped, may form the subject of another paper.

In conclusion the writer wishes to thank Mr. J. Guy W. Johnson, B.A., for help in taking some of the observations.

DISCUSSION.

DR. LOUIS KAHLENBERG: Mr. President, I would like to ask Professor Barnes how long it takes to make a determination?

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DR. H. T. BARNES: The actual determination is very quickly done, provided that you can get enough of the fluid to make a measurement and weight accurately. As soon as the electric current is turned on, five minutes or even less may be required for the attainment of steady conditions, because the calorimeter walls are very thin.

MR. A. H. COWLES: I would like to ask if it would not be possible to eliminate the thermometers entirely and pay attention to the difference of resistance in the wire when cool and when hot, thereby using an electrical means of measuring the temperature instead of using a thermometer.

DR. BARNES: I think you will find in doing that that your temperature measurements would be very inaccurate. In my measurements I spoke to you about before, the wire was about twelve degrees hotter than the water around the wire. Even when I had the water thoroughly stirred the central wire was about one degree hotter than the water. The mean temperature of the wire was a degree hotter than the temperature of the water. Therefore on a ten degree rise you get an error of nearly a degree, so that I do not think it can be made accurate.

MR. R. S. HUTTON: Mr. President, I think we ought to be very grateful to Professor Barnes for the clear exposition of the subject that he has given us. The applications of this method which Mr. Barnes has touched upon are interesting. The subject of calorimetry bears closely on that of our science of electrochemistry, and the applications of calorimetric measurements are of great value, as we are often, to a great extent, limited in calculations connected with electric furnaces by insufficient knowledge of the specific heats of the substances we have to deal with.

MR. HENRY NOEL POTTER: It has occurred to me during the reading of this paper that in the application of this method to salt solutions, the mixing of fluid which Dr. Barnes accomplished, as I understand by causing the wire to be in a spiral form, might perhaps be better effected by having the glass tube fluted and having the wire straightened and covered with a thin glass tube.

To have a spiral wire coated with an insoluble non-porous insulator would be attended with great difficulty, and it would

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seem a mechanical advantage to have a straight wire, and effect the mixing action by the form of the glass tube itself.

I would like to ask whether the cylindrical shape of the glass tube has necessarily anything to do with the accuracy of the measurement.

DR. W. R. WHITNEY: I would like to ask if the alternating current cannot be used.

MR. C. J. REED: There is one point I did not quite grasp, and that is just how the loss of heat by conduction through the wires was determined?

DR. H. S. CARHART: I should like to make one remark. One is naturally inclined to bring in his own specialty, and I want to call the attention of the Society to one fact which illustrates the accuracy with which this work of Dr. Barnes has been done. His results were found to agree with the mechanical equivalent of heat as measured mechanically within so small a quantity that the difference was entirely accounted for by assuming the electromotive force of the Clark cell at 15° to be 1.43325 instead of 1.434. The value obtained by myself and Dr. Guthe by an absolute measurement was 1.4333.

DR. BARNES: Mr. President, in reply to these questions, and first, that of Prof Hutton's in regard to the specific heat of gases. This to my knowledge has never been applied to cases of high temperature. It is obvious that the method could be applied very readily in a great many ways. I think Mr. Travers, of University College, London, made a suggestion a year or so ago, that the method could be applied to determining the specific heat of gases. Whether he has done anything since with it or not, I have not heard, but I should think that the suggestion of the measurement of high temperatures, which Mr. Hutton has made, would be an exceedingly good one, and one that would give very valuable results.

In regard to the question of the next gentleman, Mr. Potter, as to a cylindrical conductor, I have made heating wires out of platinum which have been placed through a capillary tube, and this capillary tube warmed and delicately wound up into a spiral. It could also be made to a fair degree of accuracy by putting it through a cylindrical glass rod and suitably stirring the water around it. I am sure measurements in that way could be

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obtained. Of course they could not be obtained to a great order of accuracy, but they could be made more accurately, I am sure, than by the older methods of calorimetry. Any one experienced with the older methods of calorimetry will know how very uncertain they are at the best.

In regard to Mr. Whitney's question on the use of alternating currents, I have never used alternating currents, but I do not doubt they could be employed.

In reply to Mr. Reed, the conduction from the ends of the calorimeter occasioned by the introduction of the leads into the calorimeter could be calculated approximately, but it is done best by taking readings when there is no electric heating current on at all. This takes into account the difference between the calorimeter and the room temperature.

In the case of the simple calorimeter the heat loss is determined from observations with water, and that heat loss is applied as a correction when other liquids are used. The water is flowing around the wire all the time, so that the temperature gradient of the outflow tube, where the thermometer is placed to obtain the rise of temperature, from the point where the liquid enters it to where it leaves, does not vary very much if the flow is great. In order to reduce the correction to a small quantity it is necessary to have large flows of water, or to have the flow above a certain limit. I have worked this out in my measurements for my calorimeters and I have shown that above a certain limit of flow the conduction error is negligibly small.

In reply to Dr. Carhart, I obtain the value of the Clark cell by comparing my mean result for the specific heat between 0° and 100°, obtained by the electrical experiments, with the mean value of the specific heat obtained by Reynolds and Moorby, and the specific heat obtained by Rowland by the mechanical method is almost identical with the absolute value of the Clark cell which Professor Carhart worked out at Ann Arbor. I was exceedingly delighted to see that they were in such close coincidence, because it shows that we have an accurate relationship between electrical and thermal changes.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 17, 1902, President Richards in the Chair.

A UNIT OF ELECTRICAL QUANTITY FOR USE IN ELECTROCHEMICAL CALCULATIONS.

By Alfred H. Cowles.

This paper proposes certain electrical units suggested in order to coordinate mass quantity with electrical quantity, and for use in tracing energy in its transformations accompanying chemical reactions.

Clerk Maxwell has said:

"Of all electrical phenomena electrolysis appears the most likely to furnish us with a real insight into the true nature of the electric current, because we find currents of *ordinary* matter and currents of *electricity* forming essential parts of the same phenomenon."

May we not consider electricity as some *extraordinary* form of matter?

Units are measuring tools for use in reasoning, and when we deal with the data of a special subject such as electrolysis, they should be of such convenient dimensions as not to be cumbersome.

I have found that, as a coincidence, a kilo-ampere operating for one day through acidulated water, will free two pounds of hydrogen, lacking 0.59 of 1 per cent. It will decompose what might be called a pound-molecule of any diad compound that is an electrolyte.

Five hundred amperes in one day will decompose practically, according to Faraday's law, a pound-molecule of any univalent compound.

The convenience of this close relationship suggests the idea of making it the basis of a unit, the *pound Col.* This unit would be of the same nature as the coulomb, but it has merged in it, the day, as a larger unit of time. It is also of the same nature as the "Chemic" suggested by John T. Sprague, but it seems to have advantages over the latter as it coordinates with the day of time, and as it can be defined on the basis of the international coulomb,

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and when divided by the figure 5, it falls into perfect harmony with the metric system. For practical purposes, it can be altered in its magnitude, and fitted and used in connection with any of the United States and British units of weight.[1]

In electrolysis, electrochemical equivalents of all univalent compounds call for the same quantity of electricity to effect their separation. Compounds of higher valency call for even multiples of this quantity, according to their quantivalence. Assuming that we do not know the number of molecules in an electrochemical equivalent, we may still designate that number by N, and, in that case, each molecule on being disrupted from its state of combination, parts with an electric quantity or charge whose magnitude is always $\frac{1}{N}$. This charge is positive for the cation, and negative for the anion. This definite quantity of electricity is called the molecular charge. Maxwell went further and suggested that "for convenience of description," it might be called *one molecule of electricity*, and he stated that if this definite quantity of electricity were known, "it would be the most natural unit of electricity." While this latter unit is at present hardly attainable, its multiples that agree with the various units in our tables of weights, that are used to express electrochemical equivalence of mass, are attainable and can be positively defined. Any one of them will take the place of the figure 1 in the foregoing fraction.

As we recognize the meaning of the word "valency" in electrolysis, the atomic weight of any element divided by its valency, gives the electrochemical equivalent of that element, and, as we can take any number, X, of such equivalence, we can think of an equal number, X, times the quantity of electricity that is required for one equivalent, and write the formula,

$$\frac{\text{X electrochemical equivalents}}{\text{N}} = \frac{\text{X units of electrical quantity}}{\text{N}}.$$

This formula ought invariably to express the direct equivalency

[1] A valid reason why our Col. units should not have dimensions that are even multiples by a power of ten, above the value of the coulomb, lies in the fact that the coulomb has not an even value above the electrostatic unit. With the distance that light travels in a second, as a unit of distance, the second of time and the day of time are units of distance in astronomy. It would seem of value to have electrical units that would thus coordinate with the "day." They may lead to a reduction of the mathematical treatment of the dynamics of astronomy to electrical terms and methods. Differences in gravitational potential present a striking analogy to differences in electrical potential.

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of *quantity of mass* to *quantity of electricity* in their true relationship to energy.

Chemistry starts with the hydrogen atom, the smallest unit of that which the physicist would be forced to call mass, and from it develops the table of atomic weights and the periodic law.

When a gram-molecule, or a pound-molecule is spoken of, we know its meaning. Let us for the moment ignore mass, and think of quantities of electricity as weighable quantities. In this case we can possibly appreciate the value of units that would bring this out vividly to the mind. We would then speak with the same forcefulness as though we were talking of a pound of electricity, which by simple calculation we could convert into gram, grain or ounce quantities. With a system of proper electrical units of quantity, we can do this by so selecting them as to keep the numerical value of X on the two sides of the above formula equal, while we may vary the unit of weight that measures the electrochemical equivalent.

It may be recalled that when Coulomb used his torsion balance in order to establish a unit quantity of electricity, he was doing that which was of the nature of weighing. He placed what was mechanically equivalent to a dyne of weight, in balance with the pull of a unit quantity of electricity. Newton's law of gravitation, $\frac{m \times m}{d^2}$, is of the same nature as Coulomb's law of the attraction between electrical quantities, $\frac{Q \times Q}{d^2}$.

In the light of the relationships now known, between electrolytic conductivity, osmotic pressure, vapor tension and the raising and lowering of melting- and boiling-points, it would seem to be of value to have a set of units of electrical quantities related to or dependent upon a unit quantity by volume, of hydrogen. The liter or cubic decimeter of hydrogen at zero temperature centigrade, and the mean pressure of the atmosphere at the sea-level, was recognized by Hoffman as a valuable unit of mass for use in chemical calculations. He named it the crith. Its weight has been determined with probably greater accuracy by Professor Edward W. Morley, of Cleveland, Ohio, than any other atomic constant in chemistry. He found it to weigh 0.089873 ± 0.0000027 gram at sea-level in latitude 45°. One cubic meter weighs 89.873 grams, and five cubic meters equaling

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5,000 criths, weigh in grams, 449.356. A pound equals 453.59 grams. Hence it will be seen that five cubic meters of hydrogen are within one per cent. of the weight of one pound.

We have now to show that 500 amperes of current for one day will free just this quantity of hydrogen. The international ampere is 0.1 of the unit of current of the C. G. S. system of electromagnetic units, and it is usually defined on the basis of the quantity of silver that it will deposit, according to Lord Rayleigh's determination. It is that flow of current which will deposit 0.001118 gram of silver in one second. The atomic weight of silver as compared to hydrogen is not exactly known, unless we correct its accepted present weight, making H unity, by Dr. Morley's determination of the weight of the unit volume of hydrogen. The present figure, adopted by the committee of the American Chemical Society, is 107.92. The figure adopted by W. C. Roberts-Austen, assayer of the Royal Mint of England, is 107.66. Taking the former of these two figures, and dividing the silver freed in one second by one ampere, 0.001118 gram, by it, we find the electrochemical equivalent of hydrogen for one ampere second, or one international coulomb to be 0.0000103953, and multiplying this by 500 and 86,400, the number of seconds in a day, we find that a 500-ampere current for one day will liberate 447.5315 grams of hydrogen. Again, taking the figure for the atomic weight of silver that bears the indorsement of Mr. Austen, and making the same calculation, we find that a 500-ampere current for one day frees 448.61 grams of hydrogen. As Dr. Morley found the weight of one cubic meter of hydrogen to be 89.873 grams, his determination would make five cubic meters weigh 449.365 grams, and as his figure is a trifle higher than the weight which had formerly been attributed to hydrogen, it is probable that the atomic weight of silver will eventually be corrected to 107.11, to agree with Dr. Morley's determination for hydrogen. The divergence in these figures is merely the divergence in opinion as to what is the true weight of the cubic meter of hydrogen, but if hydrogen is taken as unity in the table of atomic weights, we see that the 500 ampere current for one day, liberates exactly five cubic meters of it.

Five hundred amperes for one day equals 43,200,000 coulombs. This is the *pound Col.* It frees practically one pound of hydrogen in one day, and exactly five cubic meters. It frees exactly

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five cubic meters of any monad element when the same is viewed as a perfect gas and is reduced to the conditions of standard pressure and temperature. It frees in pounds a weight of any monad element that is expressed by that element's atomic weight. If this quantity of electricity were divided by N, the number of molecules in a pound equivalent of any univalent compound, it would then stand for a univalent "molecule of electricity," using Maxwell's illustration. It is the quantity that will free one pound electrochemical equivalent of any element.

If the pound Col. quantity of electricity be moved against a counter-electromotive force of one volt, it calls for an expenditure of 43,200,000 joules. 43,200,000 joules equal 10,396,480 gram-calories. This quantity of energy should have a name. Imagine a condenser of sufficient capacity to hold this pound Col. quantity of electricity when charged to unit potential of one volt. To thus charge it would call for an expenditure of 21,600,000 joules, and if its positive and negative electricity were permitted to again rush together, there would be an evolution of 5,198,240 gram-calories. This unit, the pound Col., divided by N, the number of atoms in five cubic meters of hydrogen can be thought of as the electropositive charge that accompanies the atom of hydrogen. The atom of hydrogen weighs one in the scheme of the classification of the periodic law. The physical properties of the elements of chemistry seem clearly to be functions of their atomic weights. If what we may think of as the mass atom in chemistry has a definite relation and equivalence to what we have called the electric atom, then temperature potential, as measured in degrees on one side, and electric potential as measured in volts on the other, are related to each other in the proportion of one volt to 22.923° C., when water having unit capacity for heat supplies the unit vessel to hold heat. It must be recalled that the capacities of different atoms for heat are approximately equal, and would probably be found to be exactly equal were it not for physical changes in the states of aggregation of masses of them. On the other side of this proposition, we may venture the opinion that the *capacity* of all atoms for electricity or electric charge is equal when we allow for their valencies, excepting as affected by the storage of intrinsic energy accompanying segregation in the formation of elementary molecules such as HH, after H is freed from combination.

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I feel convinced that a further study of the heats of combination now known for so many compounds, which merely express, in other terms, their voltages of disruption, will show us the allowance that must be made as a departure from unity, in the case of each element, for the intrinsic charge of its elementary molecule, and thereby render possible the creation of a table of apparent relative atomic capacities for electricity, similar to the table of atomic weights. With the numerals of this table known, thermal reactions or energy transformations will be read with the same ease that we now read and trace the shifting of mass in chemical reactions. The reciprocal of the voltage of disruption is the capacity of the molecule at unit potential for electric charge. A table of these reciprocals would be analogous to an obverse side of a table of molecular weights. The data for such a table is already extant, and the writer ventures the prediction that the rest will soon be solved. Considerations of this nature urge that this unit should agree with the unit volume of hydrogen. The unit which fits the pound is not so thoroughly in accord with the metric system as would be a unit to agree with the one cubic meter of hydrogen. This is freed by the 100-ampere current for one day. Its weight is a kilocrith. The unit would be a *kilocrith Col.* For purposes of pure science, this quantity of electricity would furnish an ideal unit. It is clear that, having derived one of these units, a whole system of other units may be derived from it in the same manner that we transform pounds into ounces, grains, kilograms, or grams, by dividing or multiplying by the same figure that we would divide or multiply by in order to change the pound to the larger or smaller units of weight. By prefixing the word pound, kilocrith, crith, ounce, grain, kilogram or gram, to the words Col, Colad, Colore or Cojoule, these derived units would be designated by their proper descriptive names.

The name *Col* would have advantage of resembling in sound, the name coulomb.

The name *Colad*, the corresponding unit of capacity, would resemble the name Farad.

The name *Cojoule* resembles joule in sound. Moving one Col against a counter-electromotive force of one volt, would call for the expenditure of one Cojoule, a very large unit of work, like the smaller units, watts per second, or joule. One *Cojoule* would

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be equal to 43,200,000 joules, or watt seconds. It would be equal to very nearly two-thirds of one horse-power day, or, 0.6702413 horse-power for one day, when the Col. is a pound Col. This, in turn, would equal 31,849,800 foot pounds or 44,034,287,000 gram-centimeters.

The *Colore* would be the quantity of heat evolved when one Cojoule of energy is converted into heat. The name Colore pronounced to resemble the long o in Co., would be similar to the small unit the calorie, in sound. The pound Colore would equal 10,396,480 gram-calories or 22,923 pound C. heat units. This latter figure can be used directly in converting heats of combination into voltages of disruption when the valencies of molecules are considered. The heats of combination in terms of Colores would agree numerically with the voltage of disruption of all univalent compounds, and, dividing the number of Colores expressing the heat of combination by the number of bonds disrupted, we would in all cases, secure the voltage of disruption.

The *Col.* without prefix, *would stand for the monad atom of electricity.*

That exactly one cubic meter of hydrogen should be liberated through electrolysis by one hundred amperes in one day, is startling. I cannot view this agreement as a mere accidental coincidence. One would not expect it to be a necessary consequence of Faraday's law. It is a fact that is not stated in the literature of electrolysis. My noting it might be classed as an accident. It may permit important scientific deductions. Why is it that ten electromagnetic units of current flow tick off per second just sufficient volume of hydrogen to record the day of time when a cubic meter is filled? What kind of an hour-glass is this that we encounter? May it not be one whose converging sides will act like the focused light of a powerful lens and enable us to learn of the dynamics of the atom, and measure its dimensions?

Viewing the average volume occupied per single atom of hydrogen in a gaseous state at standard pressure and temperature as a cube, our full cubic meter enables an easy demonstration that a few even multiplications starting with such cube as a unit, by 1,000 at a step, bring a volume of the exact contents of the cubic meter.

NOTE.—The value here given for the Colore is based upon 0.240658 gram-calorie, being equal to one joule, and 746 joules per second being equal to one electrical horse-power. The value of one joule is sometimes given as being equal to 0.23895 gram-calorie. It may be that the latter value should have been selected instead of the former.

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This agreement, therefore, points out to us the fact that the value of the meter is as truly based upon the atomic volume of the gaseous atom of hydrogen, for its absolute measure, as it is upon the earth's quadrant, if we take it to be one ten-millionth part of the latter. Other branches of physics have already made their contributions as to what constitutes the atomic volume of the hydrogen atom in a gaseous state. Space will not permit us to go far into the speculations that are suggested, but the writer calls attention to the following facts. The dimensions of the electromagnetic flow of current are dependent for their magnitude upon the electrostatic unit of quantity. The magnitude of the latter is determined by the value or magnitude of the dyne of force. In turn, the *dyne* may be viewed as dependent upon the mass of the earth and the mass, one gram, or of one cc. of water under standard conditions. These relationships are not arbitrary. They are all interdependent, one upon the other. During one second, the electromagnetic flow of current presumably involves the flux of 30,000,000,000 of electrostatic units through an electrolyte, and weighing the hydrogen freed in terms of dynes, it frees 0.10207 dyne weight. If this figure were an even one-tenth, we would feel that we were close to a solution. Again, it can be shown that one-tenth dyne weight of hydrogen is freed by the flux of 29,411,400,000 electrostatic units. If this numeral were a little larger to agree with the centimeters in the velocity of light, we would again feel that we were close to the solution, but it is about as much too low as our first figure is too high. The solution of the reason of this agreement will, in the writer's judgment, be found in the ratios of the velocity of light to the velocity of the earth's rotation, which is governed by the day of time, which must be considered in connection with the mass of the earth, which fixes the mean value of gravity, and is determinate of the *dyne's* magnitude, that can cause one cm. acceleration in one second's time, to the mass of one cc. of water.

One thousand grams of water fill a liter and weigh one kg., while a liter of hydrogen weighs 0.000089873 kg. This latter figure also respresents the specific gravity of hydrogen under standard conditions, with water as the basis of unity. It is, therefore, the figure which makes possible the reduction of relative weights of equal volumes of all gases, to a comparison with water as a unit of specific gravity. By the law of Avogadro, equal volumes of

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all perfect gases contain the same number of molecules, the molecular weights of all substances are directly proportional to their specific gravities, assuming them in the state of perfect gases, and they are compared on level planes of temperature and pressure. Therefore, this relationship is one that is inclusive of all the elements, and it is of such a nature as to enable the electrochemist to join hands more readily with the physicist who has already studied the thermal dynamics of gases.

While we have found the current that fills the cubic meter in one day, some Maxwell or Lord Kelvin might have told us what to look for. Let us hope that he will yet make the mathematical demonstration to show why the result is what it is.

DISCUSSION.

MR. CARL HERING: Mr. President, while the relations which Mr. Cowles gives are very curious and some of them quite interesting, I would like to express my personal opinion that they are largely if not entirely accidental. I wish it were otherwise. The weight of a cubic meter of hydrogen depends on many things besides the meter, such as temperature, barometer, latitude, distance from the center of the earth, and so on. I would like to ask Mr. Cowles what the origin of the term "col." is which he frequently uses as a prefix.

MR. A. H. COWLES: There is really no origin to it. I was simply looking for some convenient short name, and, to be honest, I thought if it were adopted, taking the plural of it, it hits my own name quite closely.

DR. W. D. BANCROFT: Mr. President, I do not pretend to know whether these relations pointed out by Mr. Cowles are mere coincidences or something more, but there is one further coincidence which may be worth mentioning. Starting with our standard gas volume, 22.36 liters (the last figure, of course, being uncertain), if you take one-half of that, you get 11.18 liters; in other words, one gram of hydrogen under standard conditions would occupy volume of 11.18 liters, and one atomic weight of silver under standard conditions, would occupy twice that. There is an exact numercial agreement between the volume occupied by one equivalent of hydrogen and the electrochemical

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equivalent of silver in milligrams. Whether that means anything I have not the remotest idea, but this numercial coincidence may be connected with some of the coincidences pointed out by Mr. Cowles.

DR. N. S. KEITH: It is astonishing to learn that the English pound about which we have had so many difficulties, which we designate as a relic of barbarism, and which we have been trying to get rid of, is an alleged, or possible, dispensation of Providence, which we have not appreciated.

MR. C. J. REED: It seems to me that these relations are exceedingly interesting, and that it would probably be of great practical use to have a unit for commercial operations, of large size, in which the ampere-day should figure as the standard. But when it comes to assuming that there is any natural or essential relation between the volume of a gram of hydrogen and the time of rotation of the earth, for instance, it seems to me that there can be no such relation in nature, that is, as an essential relation, nor any such relation as that binding the volume of a certain weight of hydrogen to the temperature at which water happens to freeze, or to the mass of matter that happens to be in the earth, or to the density of the earth, which determines the intensity of gravity. If such were the case these constants of nature would be continually changing as matter is continually falling to the earth from space outside, and so increasing its mass. It seems to me that any speculation bringing those quantities into fixed essential relations is absurd.

DR. J. W. RICHARDS: What I get from Mr. Cowles' paper is the interesting fact that a hundred amperes in a day sets free very nearly one cubic meter of hydrogen. How near it is to one cubic meter is a coincidence, purely so. Using the best data which we have at present, it comes very near. Mr. Cowles, I think, says exactly; but at least it is near enough for many commercial problems, and I think I shall remember that as a convenient means of getting the volume of hydrogen which will be set free during a day by any given current. I am firmly convinced that the coincidence is accidental. It reminds me of another coincidence which I think I discovered. I never saw it published anywhere else; and that is, while a cubic meter of hydrogen weighs 0.09 kilogram, a cubic foot of hydrogen weighs almost exactly

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0.09 ounce avoirdupois. The coincidence is true to 0.1 per cent. and is a very useful one in calculating the volumes of gases set free in chemical reactions when you want to use the cubic feet and English weights? Another interesting coincidence is that one ampere deposits one ounce of copper per day, within 0.1 per cent. This is also a very useful memorandum. I believe, however, that any linking of the electrochemical equivalent of hydrogen to the time of rotation of the earth is highly speculative.

MR. A. H. COWLES: Mr. President, I agree perfectly with you that my assertion that there is a fundamental relationship causing this agreement is highly speculative. But if you never speculate you never strike the truth on any great proposition. Now, as I view this agreement it seems to me to be a necessary consequence of a set of relationships. There may be a variation from exact agreement that is due to the errors of human beings making their measurements. If those errors cause a divergence from the fact, why, it is well to consider the thing exact, and investigate it on the basis of its being exact, and see where the investigation leads you. If you can find some fundamental cause that explains it, then you can assume that the measurements were very nearly right, and they merely ought to be corrected a trifle. That is the way I view it.

Mr. Reed made one remark in criticism which I would cite as the very reason for my suggestion that the relationship may be fundamental. Namely, he said, our units would all be changed if the world changed in its mass or changed in its velocity of rotation. That is just the point I make. They would all change in proportion. They are all interdependent upon one another in just that proportion, and the revolution of the world in the day of time is one of the factors that govern our units.

DR. W. D. BANCROFT: Mr. President, might I add one thing more? I should like to confirm Mr. Cowles' statement in regard to Mr. Reed's remark; that is, if the earth changes in mass owing to matter falling on it from somewhere else, and if that is enough to be perceptible, it will change, of course, the atmospheric pressure, and therefore change our standard volume. There is, therefore, a very definite connection between the standards we have taken and the mass and velocity of rotation of the earth.

MR. REED: In what way is the velocity of the rotation of the earth connected with it?

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Of course I can see that the addition of a mass to the earth would change gravity. What I was going on to say was that it would not change the properties of hydrogen gas. It would not change the quantity of hydrogen gas that would be liberated by one ampere-hour for example.

MR. COWLES (communicated): Since the discussion of my paper I have secured from Dr. Morley, the atomic weight of silver with hydrogen one, as based upon his determination of the weight of one liter of hydrogen. The figure thus given for the atomic weight of silver is 107.11, somewhat lower than the figures which I used. Accepting this figure as being very nearly correct, I find upon calculation that the pound Col, or 500 amperes for one mean solar day lacks just 0.59 of one per cent of freezing one pound avoirdupois weight of hydrogen. The kilocrith Col, or 100 amperes for one mean solar day liberated 0.34 of one per cent. more than that necessary to fill the cubic meter. Calculating the hydrogen freed by 100 amperes for one siderial day, or for one true revolution of the earth on its axis, the cubic meter is just filled and there is an excess of hydrogen of 0.07 of one per cent.

Independent of the electric current, I have noted the following striking agreement, which points to some kind of a connection, if it is not pure accident, between the number of seconds in a mean solar day, and the mass of a liter of hydrogen. The three values in the second column below are the values of gravity at the north pole at 45° latitude and at the equator. It will be seen that dividing 86,400 seconds in a mean solar day, by these values we secure as a mean result to within 2.4 parts in 10,000, the weight in dynes that one liter of hydrogen would show if weighed with a spring balance at the three places named.

Seconds in mean solar day.		Value of gravity.		Weight in dynes of one liter of hydrogen.	
86,400	÷	983.11	=	87,884	
86,400	÷	980.61	=	88,108	
86,400	÷	978.1	=	88,334	
Weight in grams of liter of hydrogen.					
0.089873	×	983.11	=	88.355	at pole
0.089873	×	980.61	=	88.130	45° lat.
0.089873	×	978.1	=	87.905	at equator

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September, 18, 1902, President Richards in the Chair.

PUMPS AND OTHER ACCESSORIES IN ELECTROLYTIC PLANTS.

By D. H. Browne (with drawings by L. R. Vorce).

The successful conduct of any electrochemical process depends not only upon the care with which the electrical part of the subject is worked out but to a great extent upon the mechanical questions involved and the means provided for conveying the solutions to the baths and disposing of the products of the same.

In the hope that a recital of certain deviations of my own may deter others from the same tortuous path, I have here recorded some of our struggles with pumps, heaters, and other mechanical problems.

About the worst solution I know of to handle is a hot concentrated solution of chloride of copper and nickel. If the material advantages of such a liquor be augmented by a little free chlorine, some hydrochloric acid, and a job lot of such impurities as sand, graphite, copper sulphide, metallic particles, chips of wood and bits of cotton waste, then the problem of handling such a liquor is not to be contemplated with unalloyed pleasure. Such a solution we have had for several years to pump, filter, evaporate, circulate, and electrolyze. In so doing we have accumulated certain information that may be of interest to the American Electrochemical Society.

Our first experience in this line was gained some eight years ago from a learned foreign doctor, who was then exploiting a method for the direct refining of copper and nickel from mattes. In order to handle his solution the doctor had brought with him an assortment of pumps, heaters, and filter-presses, some of which deserve mention from their antiquarian interest.

His pump was of the diaphragm pattern and consisted of a small vertical steam cylinder, through both heads of which passed the piston rod. This was coupled above to a fly wheel and below to a bronze plunger of a pump. This plunger worked in a

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cylinder which ended in a disk-shaped foot across which was stretched a sheet of soft rubber. Below this was another cylinder lined with hard rubber and fitted with ball valves and inlet and exit tubes. The bronze plunger moving in water in its cylinder communicated its motion through the diaphragm to the solution in the rubber-lined cylinder below.

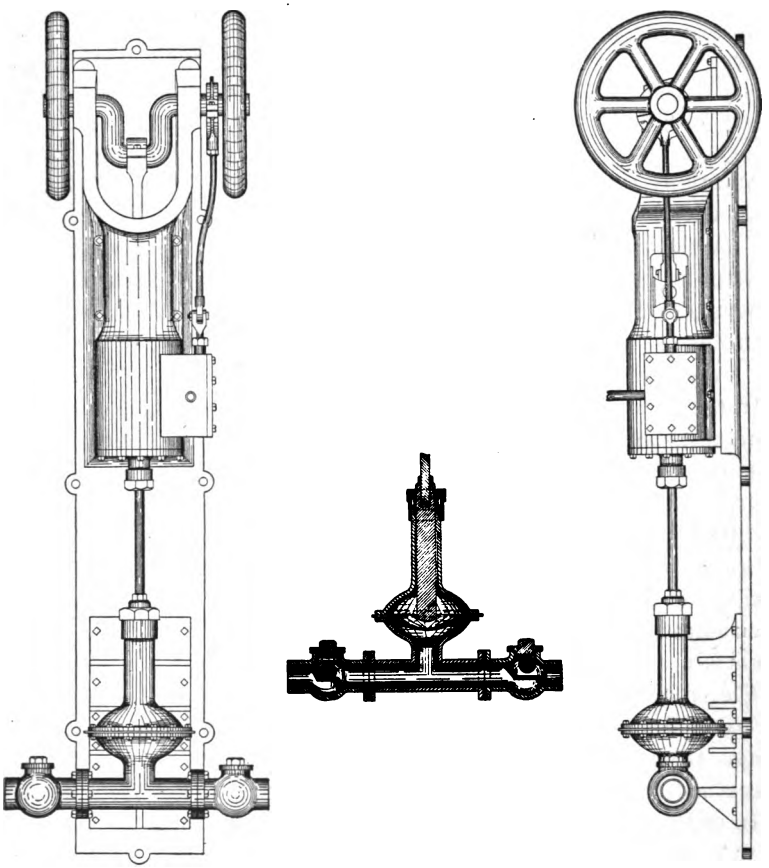

FIG. 1.

When I first saw this apparatus it was endeavoring to force through a filter-press a solution of chloride of nickel carrying ferric hydrate ; an operation I have since found succeeds best at 100-pounds pressure. In order to prevent injury to the diaphragm

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the machine was provided with a safety valve, something like a dashpot, the lid of which was held down by a lever weighted with hammer heads, monkey wrenches, and other junk. The pump worked fairly well at first, but as the pressure increased the ball valves used to stick or slip, allowing the water piston to work without load, when the fly wheel would race until the ball fetched loose with a jerk, knocking up the lid of the safety valve and squirting hydrates and chlorides over the shop.

A diaphragm pump is undoubtedly a good thing in its place, but coupled to a filter-press it reminded me very strongly of the explanation of the tides as given by one of the early church fathers. He held that these mysterious motions of the sea were caused by the alternate suction and belching of the leviathan.

In order to heat the electrolytic solutions the doctor made use of a porcelain-lined steam jacketed kettle about two feet in diameter and nearly hemispherical in shape. A white enameled paddle worked by a bevel gear kept the contents of the kettle in motion, mixing the ground matte with the various chlorides which were to effect its decomposition. This apparatus was, of course, too beautiful to last. In a few days the protective enamel coating was chipped or worn through in spots allowing the copper to begin work on the cast iron below, and the chlorine did the rest.

After the doctor had returned to his native land we were left to struggle unaided with the question of pumps. Our first venture was to discard them entirely. We wanted no moving parts, so we ordered a couple of stoneware blow-cases. When these arrived we unpacked them with great reverence. They resembled roc's eggs—save for certain knobs, cocks and flanges on one end. To protect them we placed them in straw and excelsior and sunk them in a box below the level of the floor. Nothing remained in sight but the funnel through which the apparatus was filled, and the exit pipe through which the solution was sent up to the second story. The air was admitted by a half-inch pipe which was coupled by a flat flange to the top of the blow-case. The young fellow who attended to its wants sat on the floor with his legs hanging over the pit. His duty was to fill the case by means of a flexible hose, close the inlet pipe and admit air from the air-compressor and so send up the liquor. The exit pipe, being of soft rubber, acted as an indicator by thrashing violently when

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the blow-case was nearly empty. In order to keep this quiet we put a side cock on the air line so that the moment the liquor was up we could open this cock and relieve the pressure on the exit hose. This apparatus worked very well—although it was slow—and, taking one man's time, was expensive. The question of its

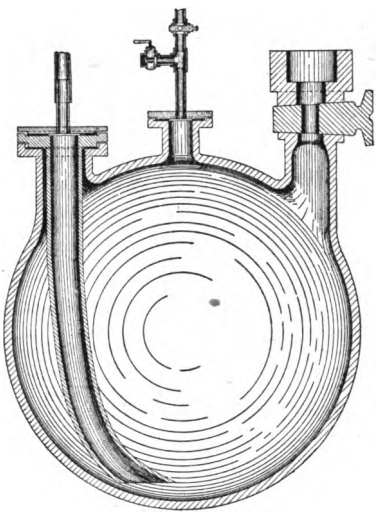

FIG. 2.

continuance solved itself. One day the blow-case seemed to be choked, and as I look back upon the occurrence my opinion is that some chips of wood must have lodged under the exit pipe. The attendant spent some time in examination and then closed the inlet cock, let on air at full pressure and, being somewhat cramped from stooping over, he laid his hand on the air pipe to help himself to his seat. The side strain thus brought on the flange was the last straw that broke the blow-case's back. It let go, and when we came to gather up the pieces we found it more thoroughly disintegrated than I had supposed possible. A large portion of it had to be picked out of the man's legs. We learned from this that a blow-case goes to pieces like the deacon's "one hoss shay," "all at once and nothing first."

Our next venture was a stoneware suction pump, over the planning of which we spent much thought. It was designed to deliver large volumes of solution at a height of six or eight feet.

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The plans of this, as made by R. C. Remmey, are shown in Fig. 3. It consists of three parts, a cylinder twenty-four inches

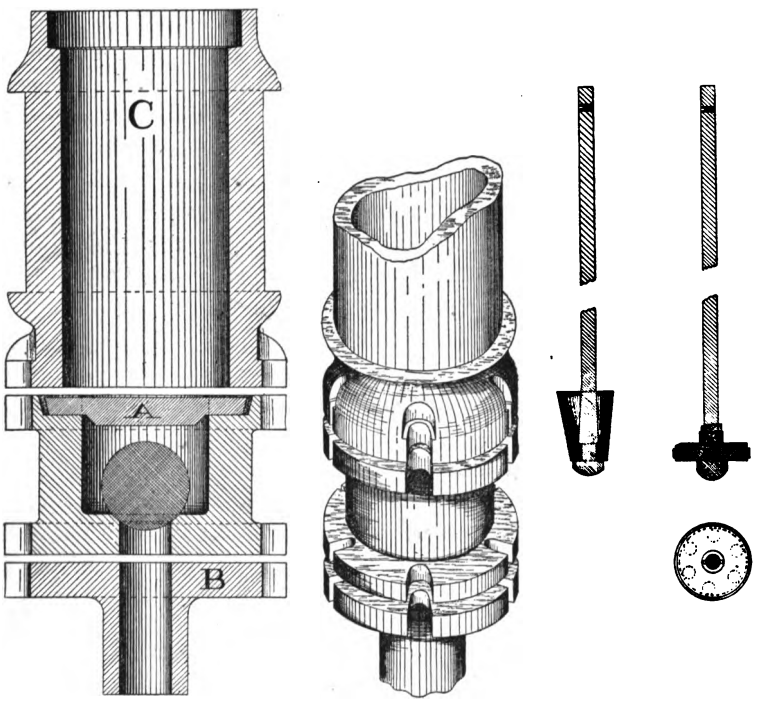

FIG. 3.

long and six inches in diameter, ground true over the lower twelve inches inside: a valve box in which a rubber ball is held in position by the stoneware piece, A, and a suction end, B, over which is slipped a heavy soft rubber sleeve. The cylinder C can be carried up several feet if necessary by means of sewer pipe, the discharge end being formed of a six-inch tee with a four-inch branch. The piston rod is turned of maple or hickory of the shape shown in the figure. The suction-pipe may be of wood, bored and like a pump log, or of heavy rubber hose if a flexible connection is desired.

The piston of such a pump was at first a source of much trouble. It was of soft rubber in the form of a cup as shown in the figure. On the down stroke the feather edge of the cup

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wrinkled and allowed the piston to slip down, while on the up stroke the weight of the solution keeps the edge tight against the side of the cylinder. This was rather a weak spot. The cup was liable to turn sideways, allowing the wear to come upon two points only, instead of bearing evenly upon its entire circumference. We finally discarded this cup and substituted a disk of wood perforated with six one-inch holes and covered by a quarter-inch sheet of pure gum rubber. This disk is best made of curly maple, the peculiar grain of which prevents splitting. A strip of pure gum three-eighths inch by three-quarters inch let into a square groove in the edge of the disk makes a snug fit against the ground porcelain. It will be noticed that the bolt grooves are all in line and are all open, so that the six bolts will hold the three pieces together. Pure rubber one-quarter inch thick is used for the gaskets. Such a pump as this is eminently satisfactory for the purpose of lifting large volumes of solution to a height of about eight or ten feet.

For pumping to higher levels it is useless, and as our solution had in some cases to be lifted twenty or twenty-five feet, we were forced to seek some better method. Our next venture was the purchase of a hard-rubber steam-driven pump, the mechanism of which is shown in Fig. 4. This was an expensive investment, but when we set the machine to work and it commenced doing its business as if nothing were easier we felt that our expenditure was fully justified. We forgot, however, that our solutions were clean and cold, as they always were in starting up. In the course of a few days, when the solution got warmed up to about 60° C., something seemed to be wrong. The pump was throwing a very small stream and examination showed that the cylinder at the compression end was swelling up as if it were growing a goitre. As the temperature was still rising it was evident that the cylinder would soon resolve itself into a sphere, so we took the pump apart, put in a new cylinder and put it to work at something that would keep it cool. Even on cold solutions we found it a delicate apparatus. The piston rings and the inside of the cylinder wear out very rapidly if there is any grit in the liquid. A clean and cold solution, no matter how acid or how strong in chlorine, can be handled with this apparatus with entire satisfaction.

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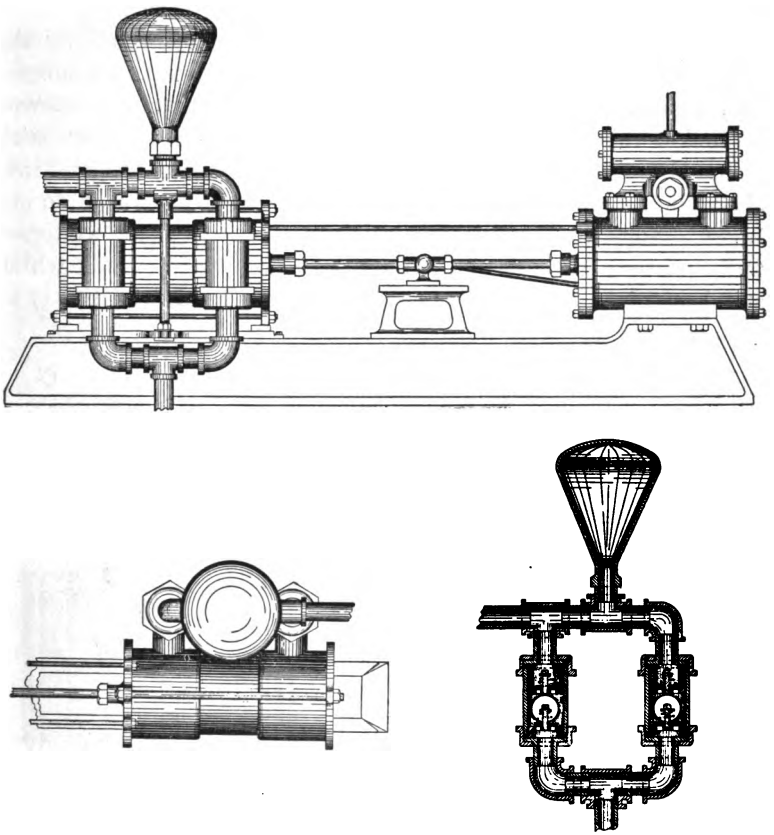

FIG. 4.

Just about this time the problem of heating and concentrating solutions commenced to trouble us. We had no faith in enameled iron, we could not use any metal, and we had not yet learned of any satisfactory substitute. Being forced back upon stoneware and steam we resolved to use steam under pressure and out of the depths of our genius evolved the apparatus shown in Fig. 5.

The solution to be heated was pumped through the crock A, overflowing at the lip to the plating baths. In this supply crock stood what we always called "the castor-oil bottle." This was of stoneware, with a flange for steam connection where the cork should have been, and an exit pipe at the bottom for condensed water. A steam guage at the inlet was kept at about twenty

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pounds pressure. This heater worked with great eclat for about three days. The third night we had finished explaining the working thereof to the night engineer and we were in the laboratory getting ready to go home when we felt a sudden jar followed by one of those sickening thuds that the journalists make such frequent use of. We rushed out to find everything resolved into chaos and blue ruin. Just what caused the explosion I do not know. Something must have sent the pressure up, for we found pieces of that bottle driven two inches into a wooden tank which stood near by. I would not recommend this style of a heater as a permanent investment.

Next day we fixed up a little apparatus which has some points of merit (Fig. 6). It consists of a circular iron tank within which stood a stoneware crock about two feet in diameter. The iron tank

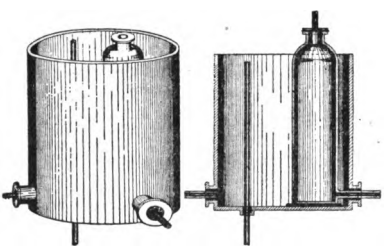

FIG. 5.

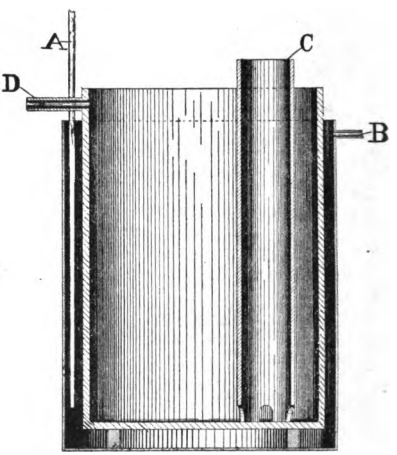

FIG. 6.

was filled with water which was kept boiling by the steam pipe A and which overflowed by the pipe B. The solution from the pump was fed into the central pipe C, out of the bottom of which it flowed upwards to the exit pipe D. This heater is very simple and thoroughly trustworthy. It will not explode under any provocation. For heating small amounts of electrolyte to 40° or 50° C., I know of nothing better.

The question of evaporating and concentrating large amounts of solution was now beginning to press very heavily upon us. After some preliminary tests we devised a concrete evaporating pan which worked for several months, more or less, satisfactorily.

The base of this evaporator was built of brick, the top course being laid in cement and a cement coat with a slight slope to the

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front was laid over the top of the brickwork. On this platform was built a shallow concrete pan with sloping sides as shown in Fig. 7. A wall down the middle divided this into two compartments, each of which was nine feet long, two feet wide and six inches deep. These communicated with the opening in the party wall. The compartments were covered by heavy tiles

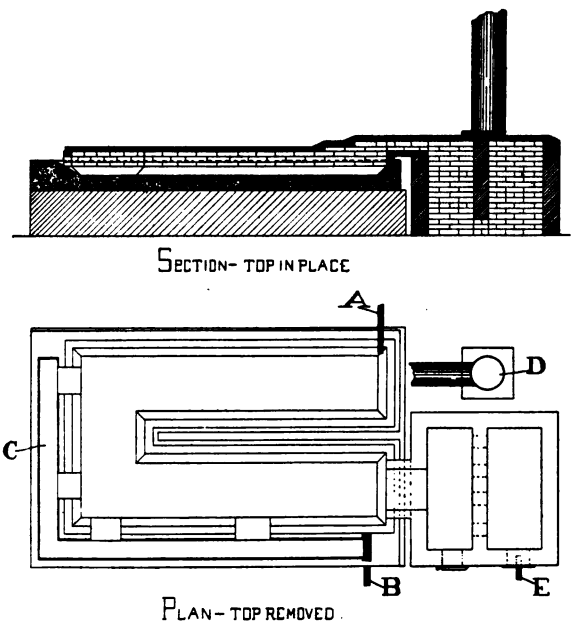

FIG. 7.

as shown. The solution flowed in at A and out at B, while any crystals settling out are raked off the bottom up the sloping sides to the trough C. The chimney D assists in drawing a current of hot air from the brick oven heated by the oil burner E.

This apparatus worked for several months and served its purpose in proving the principles involved. One trouble, however, was the coating of the solutions with a floating layer of crystals, and the other was the cracking of the concrete due to alternate heating and cooling.

The trouble given by the coating of salts covering the surface of the liquid suggested to us an idea of an evaporator in which

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a very thin film of solution is continuously exposed to a stream of hot air. We drew up plans for the rotating evaporator as shown in Fig. 8.

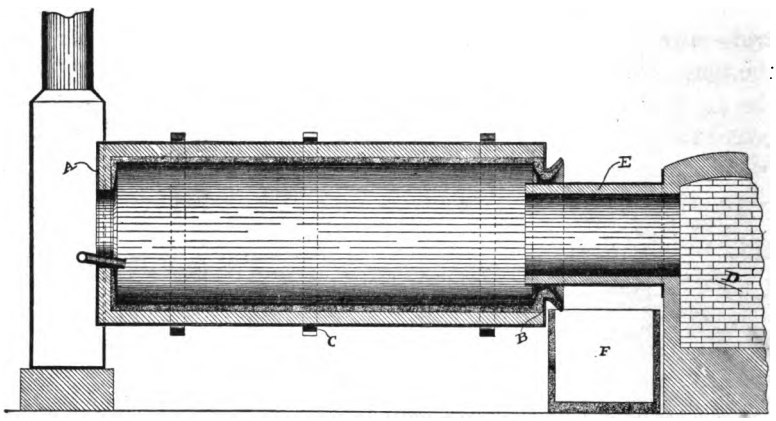

FIG. 8.

This machine, with few alterations, has been in use for two years and has proved entirely satisfactory. It consists of an iron shell fifteen feet long and six feet in diameter, closed at the upper end by a circular lip A, and at the lower end by a shallow lip B. This shell is lined with bricks and cement and is rotated by the peripheral driving gear C. An oil burner in the brick furnace D to one side produces a current of hot air which, entering the evaporator by the sleeve E, passes along the top of the arch, meeting there a film of liquor which is continuously dragged up from the pool. The solution flows in continuously through the pipe and out continuously over the lip through a ring opening about one inch in diameter around the air sleeve. Any crystals separating out are carried in suspension into the tank F where they settle out while the solution passes on towards the pump pit. With this machine, at first, we used a fan to draw the air through, but experience showed that better results are obtained by checking the air flow to such an extent that the exit gases are nearly saturated with moisture. We can now evaporate off 1000 liters of water per hour with a consumption of 90 liters of oil. It is evident that economy would be secured by building the shell much longer and of smaller diameter.

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As a solution of the problem of the concentration and evaporation of electrolytic solutions such as we use I can thoroughly recommend this apparatus.

It must not be supposed that during our experiments with blow-cases and with suction-pumps we had forgotten our old standby, the stoneware force-pump. As made in those days, a pump came in three major and six minor pieces which were assembled by means of iron collars drawn up by an infinity of small bolts, nuts and turn-buckles. These being of iron were very readily corroded by any copper solution that might leak

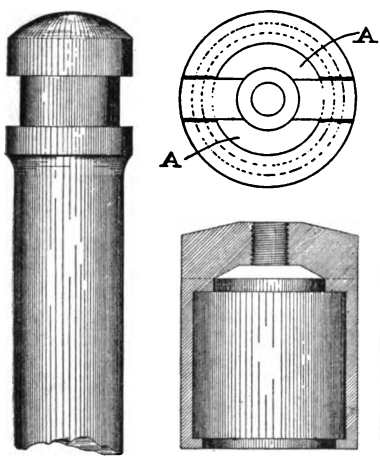

FIG. 9.

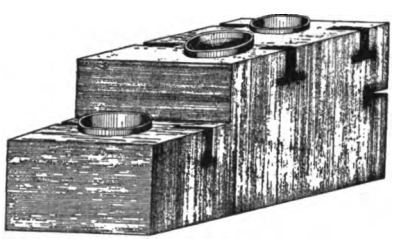

FIG. 10.

over them, and the breaking of any one threw a cross strain on the others which ended in a broken flange and a disabled machine. The German pumps have, even to this day, a most remarkable method of piston fastening. On the head of the stoneware plunger is a sort of mushroom or cap, below which is a circular groove. It is intended that a collar shall be drawn around this groove and the collar in some way secured to the plunger rod. For this purpose we devised various cast-iron clamps, one of which is shown in Fig. 9. This was set over the head of the piston and cement was poured in at the openings A to make a snug fit. We used this device for some months until one day we accidentally broke the top off the piston. Our dismay was changed to joy by the discovery that the piston was hollow. We at once shoved the plunger rod down to the bottom of the hole, poured in some cement and the next day the pump was as good as ever. After that we always broke the mushroom off the piston.

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This was indeed an improvement, but as yet we had no way of getting rid of the iron fastenings by which the pump was held together. Accident showed us that a broken delivery pipe, if tied up in splints and set in a plaster cast, like a broken leg, was still capable of doing duty. This led to further experiments on the virtues of cement, the use of which was extended until the entire pump was encased in concrete. This proved entirely satisfactory. Our present procedure is to assemble the three main parts of the pump in a box, laying the pieces close together without gaskets between. Around these pieces granite concrete is rammed and the block allowed three or four days to harden before removing the box. To provide for the bolts which hold down the valve checks and the piston gland, short pieces of iron pipe may be laid in the box before the concrete is rammed in, or better still, T-shaped slots may be provided in the concrete by suitable wooden forms nailed against the side of the mould (Fig. 10).

The three-piece pump, so mounted, is practically one solid block of stone. It requires no fastening, can be laid on the floor anywhere, and is very readily lined up beneath a driving shaft. In one respect, this old style three-piece pump is more convenient than the one-piece model which I shall refer to later. That is, the side outlet at the delivery end, a form somewhat easier to manage than the top outlet.

As a gasket for this style of pump I have found common felt well soaked in P. & B. paint is a good substitute for soft rubber. Care should be taken that the balls are of suitable size and weight since a ball valve that will settle quickly in water will act very slowly in solutions of high specific gravity.

About a year ago we had made by Graham, of Brooklyn, several pumps of the style shown in Fig. 11. Being in one piece it is very easily mounted in a concrete block. One end is provided with a skeleton ball check which acts both as a check and discharge opening. The exit pipe is coupled to this by a flat flange and hard rubber nipple as shown in the figure. To hold down this check and the piston gland we use a heavy cast-iron plate with two claws on each side against which the bolt heads or washers can be drawn up. This makes a very compact form of pump mounting which serves our purpose admirably.

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As suction-pipe we use either a section of a wood pump log drawn tight against the lower part of the pump body or a hard rubber flange and nipple coupled to a length of flexible hose of sufficient wall thickness to withstand the collapsing strain. In some cases we use a special suction-pipe of stoneware made by Remmey, as shown in Fig. 12. All these forms are serviceable according to the kind of solution to be pumped. For discharge pipe we use almost exclusively a permanent concrete main. This is made by passing a small sewer pipe through a larger one so as to break joints, the space between the pipes being rammed up with good small concrete. The inner pipe is brought

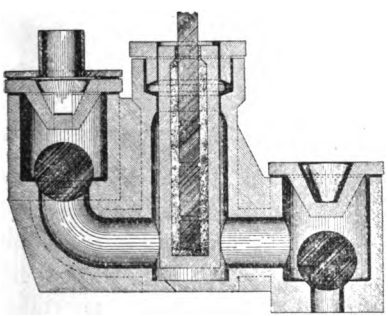

FIG. 11.

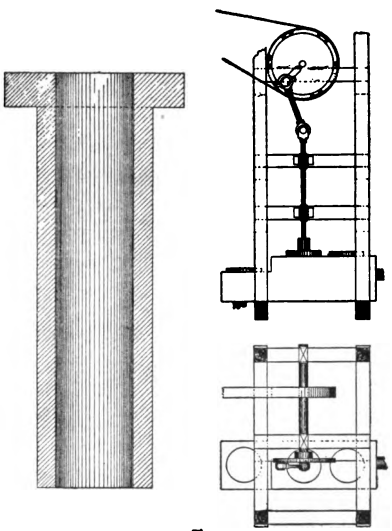

FIG. 12.

by means of a quarter bend through a tee branch in the outer pipe, the space between being filled with cement and troweled to a smooth finish. Against this a rubber gasket is laid and then by a collar around the sewer pipe a hard rubber flange and nipple is drawn tightly back against the inlet of the inner pipe. A short flexible connection is now very easily made with the discharge end of the pump.

Such permanent connections as these we have found greatly superior to soft rubber for exit pipes.

The mounting of these pumps is very simple. As shown in Fig. 12 it requires four uprights which carry the plunger rod guides and which support the bearings of the counter shaft, the center of which must be exactly above the center of the piston. By means of the slotted face plate the length of pump

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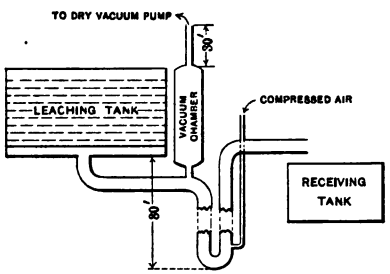
stroke may be regulated, and by using a clutch pulley on the sprocket chain any pump on the line can be stopped or started without reference to the others.

DISCUSSION.

DR. N. S. KEITH: Mr. President, I would like to describe a system of pumping such liquids which I have adopted and used to some considerable extent. I will make a sketch upon the blackboard which will assist me in describing the system.



There is here represented a leaching tank from which it was desirable to extract the liquid by a vacuum produced underneath. The various pumps for producing a vacuum have about the same trouble with the same kind of liquids, as described in the paper. My desire was to be able from one source to do all the pumping of the establishment, and that by the means of compressed air. But how to produce a vacuum by means of compressed air and convey the liquid to another point was a problem that had to be solved. It was solved in this way and worked very satisfactorily, except as to the endurance of the material from which the pipes were made. But those pipes can be made, and will be made, of a suitable material, very possibly, or probably, of wood, saturated so as to resist the intrusion of liquids which would rot them.

A line of pipes is here represented passing from the bottom of the leaching tank to the receiving tank. An exhaust or vacuum air pipe is represented. This pipe extended above the top of the liquid as it would stand in the tank to about the height of thirty feet. In the upright pipe was a chamber to receive any liquid which, by any accident, should be drawn up. A branch of this pipe then descended into a well to a distance exceeding thirty

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feet, say eighty feet. When the solution came to the lower bend and the air struck it, it was elevated to the receiving tank. A vacuum was thus produced in this pipe above the liquid flowing through it. This vacuum was preserved constantly by a dry vacuum pump. The vacuum pump, a very small one by the way, was necessary to remove air and gases from the liquid. There were various other methods, or arrangements, for moving liquids by means of compressed air. The compressed air was also used for agitating solutions and elevating them to a small distance, say one or two feet, at the same time from tank to tank where circulation was produced. Also for pumping 250 gallons of water per minute from an artesian well. All that is necessary is to get pipes that are made of an enduring material. The general practice of highest economy in the use of the air-lift calls for a submersion of the air pipe below the permanent surface of the liquid of twice the height, or one and a half to twice the height, to which the liquid is to be raised. If liquid is to be raised ten feet then the submersion should be at least fifteen feet; better, twenty feet. Then the pressure of the liquid in the down-cast leg of the inverted siphon keeps the air bubbles from coming out of it, and allows of the elevation in the upcast leg. I have pumped from artesian wells, in one particular case, where the elevation was fifty feet; the submersion was a little over one hundred.

MR. CARL HERING: I have used the well-known air-lift pump in a number of cases with some success; it is extremely simple, and avoids making a hole in the bottom of the tank. A tube is run down into the liquid and air bubbles are forced into the bottom; these rise in the tube and carry the liquid up between them. The action of that pump, however, is rather peculiar; one might try it without success, yet with a slight change it may operate very nicely.

MR. W. MCA. JOHNSON: I would like to give a few points which I have picked up in the work I have done, and from examining other chemical works. In my opinion there is nothing much better for raising non-acid solutions from one level to another than a compartment made of concrete, reinforced on the back by expanded metal. By the use of compressed air the solution can be raised from this tank to any height desired. In the

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case of copper refining it is very necessary to thoroughly aerate the solution, for the reason that when it is thoroughly aerated, the supersaturated air causes certain actions which purify the solution and change the cuprous copper into cupric. If, however, it is not desired to thoroughly aerate the solution the same apparatus can be employed by using a vacuum instead of compressed air. This, of course, limits the distance to twenty feet or over.

As a simple means of raising a solution in case it is indifferent whether the solution is made slightly more dilute, there is nothing better than the so-called blow-jack, or steam injector. This has the advantage that it can be used in very small units and on very small vats. It, however, is uneconomical in the use of steam, as compared with the other two methods to which I have alluded.

PRESIDENT RICHARDS: I wish to remark in connection with this paper that the importance of these mechanical contrivances should not be underestimated; that the ideas of electrolysis originating with the chemist frequently owe their commercial practicability to the mechanical contrivances which the mechanical engineer introduces, and such papers as these are extremely welcome to the Society.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1902, President Richards in the Chair.

SOME PHENOMENA OF ELECTROLYTIC CONDUCTION.

BY C. J. REED.

When an electric current traverses an electrolyte, there is always produced at the terminals of the electrolyte, that is, at the surfaces where the current enters and leaves the electrolyte, a specific kind of chemical change, *viz.*, a decomposition or a combination, in which the affected substances undergo a change of chemical valence. The valence of the substance affected at the cathode is always reduced and that of the substance affected at the anode is always increased. Nowhere, except at the terminal surfaces, is there any change of valence. The word "valence," to the chemist, has a certain very definite meaning, and represents the combining power of an atom or group of atoms in any given combination.

In ferric chloride, for example, one atom of iron is combined with three of chlorine into a definite compound having distinctive properties, while in ferrous chloride one atom of iron is similarly combined with two atoms of chlorine. In ferric chloride the iron has a valence of three, in the ferrous compound, a valence of two. The chlorine in both cases has a valence of one.

In the body of an electrolyte and at the junction of two electrolytes there is never any change of valence caused by an electric current, but at each junction of an electrolyte with an electrode there is always a change of valence proportional to the quantity of electricity (current and time). The reduction of valence at the cathode always equals the increase of valence at the anode.

From the standpoint of the chemist a compound is chemically *dissociated* only when its components are separated and the combining affinities overcome. When that occurs the valence of the components is considered zero. Thus Na and Cl in the free or separated state cannot be said to have valence, but when combined into NaCl each has a valence of one.

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According to the theory of *electrolytic dissociation* there is another kind of separation or dissociation of the components of a compound, which takes place without any change of valence. It is a kind of spontaneous separation which occurs when the compound is merely dissolved in some other substance. This kind of dissociation or separation does not require a reversal of the energy change which takes place during combination and is not a *separation* in any ordinary sense. It is a separation by definition only. To dissociate or decompose a compound already *electrolytically dissociated* (dissolved in water, for example), requires the same processes and the same expenditure of energy as to decompose the same substance before it is electrolytically dissociated, excepting only the energy of dilution, which is always comparatively small.

The mechanism of this theory of electrolytic dissociation is illustrated in Fig. 1, which shows the structure of an electrolyte according to this theory. The two electrolytic components of a

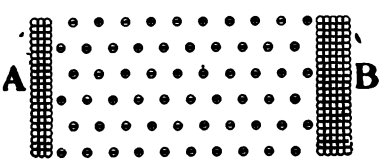

Fig 1

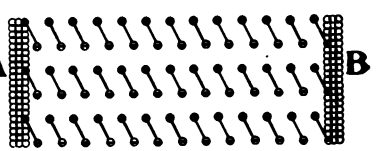

Fig 2

compound, or the ions, are represented as being individually free and capable of moving independently and with different velocities in opposite directions, impelled only by the directive influence of two oppositely, electrostatically charged electrodes, *A* and *B*. The ions marked "+" are supposed to move in one direction with a certain velocity and those marked "—" are supposed to move in the opposite direction with a velocity which may be very different. Fig. 2 represents in a similar manner the structure of an electrolyte according to Faraday. The two ions or components into which the electrolyte is decomposable, are, in this case, united in pairs into molecules by chemical affinities, which can be overcome only by the expenditure of energy.

According to this theory the molecules themselves are free to move or rotate in any direction, but the component ions are not free until the molecules are broken up or decomposed. This can

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be accomplished only by the proper application of an amount of energy equal to the energy evolved by these ions in combining. According to Faraday's theory the ions are separated from combination only at the terminal surfaces of the electrolyte, the residual components of the molecules or opposite ions being simultaneously neutralized by an interchange of molecular components in a series of molecules extending from one electrode to the other. The positive and negative components of adjacent molecules exchange partners in this process without actually becoming free or suffering a change of valence at any time. Faraday's conception was that the movement of ions through the electrolyte is caused by the chemical changes produced at the electrodes and the consequent interchange of molecular components and rotation of the resulting molecules. The elimination from or introduction into the electrolyte of matter as ions, is, therefore, the direct cause of the motion of ions through the electrolyte, each ion moving in the direction necessary to enable it to either fill a vacancy left by the elimination of a similar ion at an electrode or to make room for a similar ion introduced at an electrode.

According to the theory of electrolytic dissociation, on the other hand, the movement of the ions is due to the direct influence of electrostatic charges, causing them to move in specific and opposite directions. It is this independent movement or migration of ions which causes the chemical changes at the electrodes, instead of the chemical changes causing the migration.

The object of the experiments about to be described was to determine the applicability of these theories to the electrolysis of electrolytes in series, when the rapid mixing of the electrolytes is prevented by the interposition of partitions of porous earthenware.

The fact has long been accepted and amply proved that electrochemical actions affect only the electrodes and electrolytes which actually conduct the current; that the insertion of an inert substance, even a metallic conductor, into the body of an electrolyte has no effect on the process of electrolysis, whatever may be the nature of that process, provided the current does not actually enter or leave the interposed body. The process of electrolysis cannot be interrupted or altered by the insertion of a body, which merely reduces the mechanical cross-section and increases the mechanical length of the electrolyte.

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The mechanical separation of different electrolytes by inert, porous partitions may, therefore, be very effectively accomplished without altering the nature of the electrochemical process.

Let us assume that in Fig. 3 we have two electrodes, *a* (anode) and *c* (cathode), in a suitable containing vessel, which is divided into three compartments by the porous partitions, *P* and *P'*. The anode compartment is filled to a convenient level with a solution of $CuSO_4$ of sp. gr. 1.17, slightly acidulated with H_2SO_4 and the other two compartments are filled to the same level with H_2SO_4 of sp. gr. 1.17. An electric current is then passed through the system from the anode, *a*, to the cathode, *c*.

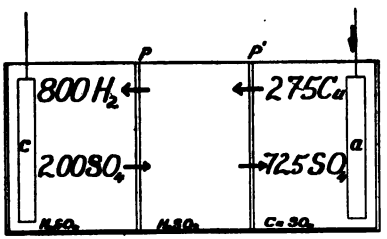

Fig. 3

According to the theory of electrolytic dissociation there are, in the cathode and middle compartments, H_2 and SO_4 ions, and in the anode compartment, Cu ions, SO_4 ions and some H_2 ions, all capable of independent migrations with different velocities. The SO_4 ions all move towards the anode, *a*, and the H_2 and Cu ions move towards the cathode, *c*. Let us assume that in a given time, with a fixed current, the total number of bivalent ions crossing any arbitrarily assumed section of the electrolyte is 1,000, as for example, one surface of the partition, *P*. The total number of bivalent ions crossing any other section of the electrolyte, as that of one surface of *P'*, will also necessarily be 1,000. The ions on both sides of *P* are H_2 and SO_4 in equal numbers. The ions on the cathode side of *P'* are also H_2 and SO_4, while the ions on the anode side of *P'* are chiefly Cu and SO_4 with a few H_2. Considering now only the current transported by the $CuSO_4$, we should have, according to the theory of electrolytic dissociation, 275 Cu ions entering the middle compartment from the anode side and 200 SO_4 ions entering from the cathode side, while 725 SO_4 ions leave at the anode side and 800 H_2 ions leave at the cathode side. We should have, therefore :

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Total number of ions leaving middle compartment		1525.
Total number of ions entering middle compartment		475.
Ratio of ions leaving to ions entering.....		3.1
Total number of molecules of H_2SO_4 taken from middle compartment		525.
Total number of atoms of Cu introduced to replace hydrogen removed		275.
Total ionic volumes removed..... ...		1050.
Total molecular volumes removed.....		525.
Total atomic weights introduced:		
$200 \times 96 = 19{,}200$		
$275 \times 63 = 17{,}325$		36,525
Total atomic weights removed:		
$800 \times 2 = 1{,}600$		
$725 \times 96 = 69{,}600$		71,200
Total net decrease in weight of middle compartment.....		34,675

We see, therefore, that according to the theory of electrolytic dissociation, both the volume and the weight of the solution in the middle compartment should rapidly decrease.

The facts, however, are exactly the reverse. Immediately on closing the circuit and causing a current to flow through the apparatus, both the volume and the weight of the solution in the middle compartment begin to rapidly increase and continue to increase at an apparently uniform rate as long as the current flows. Even with a current of about 1/2 ampere per square inch of cross-section of electrolyte, the increase in volume amounts to 1.7 cc. in one hour.

These results were first arrived at in a qualitative manner accidentally while another phase of the problem was being investigated. The increase in volume was first noticed in several experiments having other objects in view and performed with apparatus not well adapted for this purpose. It was then decided to construct the apparatus shown in Fig. 4 and study the phenomenon under more favorable conditions.

Fig. 4 represents a longitudinal vertical section of the electrochemical cell of special construction used in the experiments.

T represents a glass tube $1^1/_4$ inches in diameter and 12 inches long, closed at the ends by rubber stoppers, A and B, through which pass wires, W and W', terminating in electrodes, E and E'. On the upper side of the tube T is a row of small branch tubes, 1, 2, 3, 4, 5, and 6, open at the top and connecting below

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with the interior of the tube. On the other side there are also six other branch tubes similarly connected and open at the lower end. The twelve branch tubes have each a diameter of a quarter of an inch, and a length of two inches. The tube T is divided

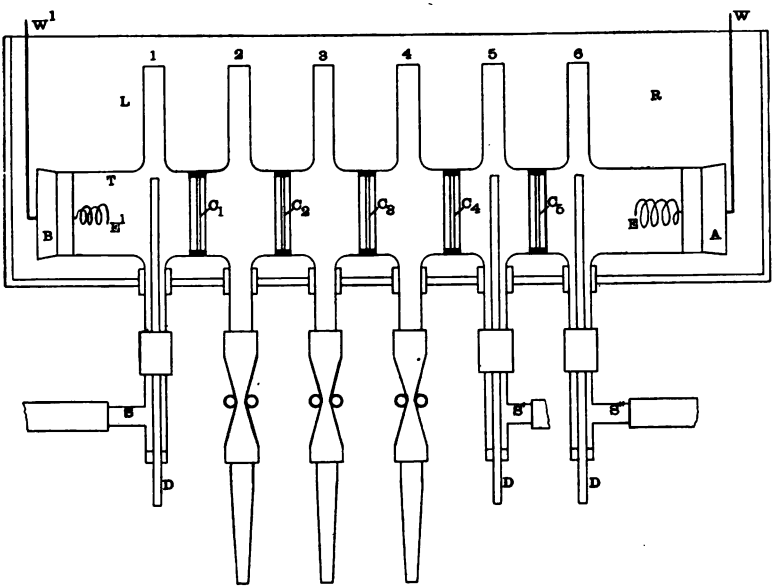

Fig. 4

into six compartments corresponding to the six pairs of branch tubes, by means of partitions of porous earthenware, C_1, C_2, C_3, C_4, C_5. Each porous partition is cemented into a hard rubber ring with asphalt varnish. Outside of the hard rubber ring there is a soft rubber ring, which fits tightly into the tube.

The apparatus is enclosed in a rubber cell, R, the lower row of branch tubes projecting through the bottom and being fitted with perforated stoppers. In operating the apparatus, the cell R is filled with a constant temperature bath to a point above the tube T. The lower branch tubes are provided either with pinch-cocks or circulating apparatus, as shown. The circulating apparatus shown in compartments 1, 5, and 6 comprises a vertical drain tube, D, extending to any desired height in the compartment,

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and a supply tube, S, for delivering the electrolyte into the bottom of the compartment.

The porous partitions were ground to a nearly uniform thickness of 1 mm. The apparatus was tested for leakage by filling the alternate compartments with water and allowing it to stand, and was found to be tight.

It will be sufficient for the purpose of this paper to give details of only a single experiment of each kind, with the understanding that the results obtained were thoroughly corroborated by other experiments and with a variety of apparatus.

Compartments 2, 3, and 4 were filled to the index level L with sulphuric acid of specific gravity, 1.169 at 16° C., as determined by weighing. This solution contained:

H_2SO_4	23.34 per cent.
H_2SO_4 calculated from specific gravity tables of Lunge and Isler	273. mgr. per cc.
SO_4 calculated from specific gravity tables of Lunge and Isler	268. " " "
SO_4 found by analysis	270.5 " " "
$BaSO_4$ precipitated	656.5 " " "

Compartments 1, 5, and 6 were filled to the index level with a solution of $CuSO_4$ of specific gravity 1.171, slightly acidified by H_2SO_4. This solution contained:

CuO	88. mgr. per cc.
SO_4	114.1 " " "
H_2SO_4, free	7.25 " " "
SO_4 in free H_2SO_4	7.1 " " "
Total $BaSO_4$ precipitated	277. " " "

In compartments 1, 5, and 6 the proper level was maintained by regulating the flow of solution through the circulatory apparatus. In order to prevent any practical change of composition of the electrolyte in these compartments a stream of the solution was supplied to each by the tubes s, s', and s'' from a reservoir containing 30 liters of solution, the pressure being regulated, by an apparatus not shown, so as to maintain the proper level constant. The tubes s, s', and s'' were very long and the leakage of current through these tubes and the reservoir was negligible.

The porous partitions were first thoroughly soaked with the solution of H_2SO_4 and compartments 2, 3, and 4 were filled to the index level L. The $CuSO_4$ solution was then allowed to flow at

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such a pressure as to maintain the proper level. This required a stream of about 5 liters per hour.

The acid solution was run into compartments 3 and 4 from burettes, and the volumes measured.

The measured volumes were:

	cc.
No. 3	20.4
No. 4	22.13

Electrodes of coiled copper wire were used and a copper sulphate voltameter was inserted in the circuit.

When everything was in readiness and the temperature of the apparatus brought to 9° C. by cold water in the cell R, a constant current of 0.57 ampere as shown by the ammeter was passed through the apparatus in the direction indicated by the arrow for a period of ninety minutes.

Weights of the voltameter electrodes at the beginning:

	Grams.
Cathode	25,737
Anode	37,242

Weights of the voltameter electrodes after ninety minutes:

	Grams.
Cathode	26,724
Anode	36,202

	Grams.
Increase in cathode	0.987
Decrease in anode	1.040

Ampere hours determined by cathode:

$$\frac{0.987 \times 0.02729 \times 63}{2} = 0.848 \text{ ampere-hour.}$$

Current during ninety minutes $\dots\dots \frac{0.848}{1.5} = 0.565$ amp.

Current measured by ammeter $\dots\dots$ 0.57

The level of the solution was maintained in compartment 4 by removing solution from time to time as the volume increased. The volumes removed and times of removal were as follows:

Time in minutes.	Amount removed. cc.
9.0	0.2
14.0	0.2
17.5	0.1
21.5	0.1
24.0	0.1
28.0	0.1
30.0	0.1

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Time in minutes.	Amount removed. cc.
34.0	0.1
37.0	0.1
41.0	0.1
44.0	0.1
48.0	0.1
50.0	0.1
55.5	0.1
60.0	0.1
63.0	0.1
65.0	0.1
68.0	0.1
71.0	0.1
75.0	0.1
78.0	0.1
81.0	0.1
85.0	0.1
88.0	0.1
90.0	0.1
Total volume removed	2.7
Total, final volume	24.83

	Grams.
Total weight of solution removed	3.15
Total final weight of No. 4 solution	29.66
Total initial weight of No. 4, 22.13×1.169	25.87
Total increase in weight	3.79
Sp. gr. of vol. added during electrolysis $\frac{3.79}{2.7}$	= 1.40
Final sp. gr. of solution $\frac{29.66}{24.83}$	= 1.195

ANALYSIS OF FINAL SOLUTIONS.

Compartment No. 4.	Mg.
CuO, total	500.0
Cu, total	398.0
CuO per cc	20.1
Cu per cc	16.0
$BaSO_4$ precipitated, total ÷ 10	1472.50
SO_4 precipitated, total	6067.
Total SO_4 (calculated) 22.13×268	5931.
Total SO_4 increase	136.

These results show conclusively that the volume, density, and weight of the solution in compartment 4 increase, although the theory of electrolytic dissociation requires that they should decrease.

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The total quantity of SO_4 in compartment 4 increases, while, according to the theory of electrolytic dissociation, the SO_4 should rapidly diminish.

There was no change in the volume of the solutions in compartments 2 and 3 and no trace of Cu in either of them.

	Grams.
The final weight of the solution in No. 3 was	23.6
Initial weight (calc. from the volume 20.4×1.169)	23.85
Apparent loss	0.25

In another experiment, compartment 4 was filled with $CuSO_4$ solution and all other compartments were filled with H_2SO_4 solution. The copper electrodes were replaced by platinum plates 1 inch wide and 4 inches long. In this case we have a body of $CuSO_4$ between two bodies of H_2SO_4.

There was in this experiment a slight increase in the volume of the H_2SO_4 in compartment 3 and a slight decrease in the volume of the $CuSO_4$ in compartment 4. The current was of the same strength and in the same direction as in the preceding experiment, but was continued 105 minutes instead of 90. During this time there was an increase in the volume of No. 3 of only 0.35 cc. and a decrease in the volume of No. 4 of only 0.24 cc. The total quantity of Cu transported into No. 3 was only 191 mg., corresponding to 163 mg. for ninety minutes; whereas, in the previous experiment, 398 mg. were similarly transported in ninety minutes, although the conditions were the same in both experiments, except that in the latter the electrodes were Pt instead of Cu and the solution adjacent to the electrodes was H_2SO_4, instead of $CuSO_4$.

These facts indicate that the so-called migration constant is not a constant, but depends on the nature of the chemical reactions occurring at the electrodes, on the nature of intervening electrolytes and the character of their junctions.

In order to determine the effect of osmosis alone on the same solutions in the same apparatus, compartment 4 was filled to the index level with the $CuSO_4$ solution and the remaining compartments with the H_2SO_4 solution. The apparatus was then allowed to stand at a temperature of 9° C. without current.

At the end of ninety minutes there was no change of level in any of the compartments, and no copper had diffused through the walls into the adjacent compartments.

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DISCUSSION.

MR. W. MCA. JOHNSON: Mr. President, I did not hear any mention of the voltage, across the terminals of the cells, and whether there was any rise in temperature in the solution during the experiment. I believe he operated at a current density of seventy-two amperes per square foot. This certainly, in that time, would give rise to certain heating effects and increase the effects noticed.

MR. H. N. POTTER: I do not wish to take up the gauntlet which Mr. Reed has thrown down, at this short notice, but it would seem that any attack on the dissociation theory must take account of the phenomena which are not electrical, which are produced by the solution of a salt. I refer to the physical effects of lowering the freezing-point, and elevating the boiling-point. It was exactly these considerations that led to a change in former theories, when it was shown that these effects distinguish electrolytes from non-conducting solutions.

MR. CARL HERING: I am hardly prepared to discuss this paper, but it seems to me that all that it shows is that Mr. Reed's determination of these migration velocities in this particular experiment is different from the migration velocities determined by those experimenters who obtained the original figures. Hittorf, who determined a number of migration velocities, published a note a short time ago acknowledging that some of them were based on wrong assumptions, and that he found that the nature of the diaphragm made a great difference in these transport numbers; it may perhaps be assumed, therefore, that those numbers are not fixed as definitely as Mr. Reed seems to think they are. I do not think that his experiment should be accepted without question as a proof that the dissociation theory does not hold. However, I do not wish to appear as a defender of the theory, either.

MR. A. H. COWLES: It is almost impossible to criticize an experiment like this, off-hand but I would only suggest that if Mr. Reed studied how much the water would change in level on two sides of the porous partition without any current flowing, he would find it would assume a difference of level with a difference of concentration on the two sides. Now, the pressure that could

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thus be created if one side of the partition were confined, would be the measure of the voltage. Pressure inside of the partition could be likened to a difference of gravitation potential, and that must be taken into consideration on Mr. Reed's part, and not alone the flow of the current during the course of the experiment.

MR. POTTER: It appears to me, looking at the figure, that the diaphragms are about 1" apart, and the tube about 1" in diameter. In liquids that are not stirred, we know that the heat losses are very gradually taken up by a bath of that kind, and it would be reasonable to suppose, that the center of that tube was considerably hotter than the surface of the compartments. The structure there shows a very neat thermometer. We have a large volume, and a narrow neck. Any slight elevation in the average temperature of the portion inside the tube, over that of the bath, would cause the liquid to shoot up the stem. In would therefore seem that it might be well that the experiment be repeated with accurately reading thermometers, set at the center of the cell.

In this connection an observation occurs to me that I made some time ago in connection with a "Simon" interrupter, in which there is a very small hole. I found that the water rose in a glazed porcelain cup separating the electrodes, no matter in which direction the current passed through the interrupter. The interesting fact is, that the liquid rose in the cup, obviously not owing to electrolytic action, but probably due to heat.

In the case before us we have a structure which is full of small holes. Of course the voltage is not known to be sufficient to produce the disrupting gaseous effects produced in the Simon interrupter, at the same time the experiment does not seem to be quite free from suggestions of error.

PRESIDENT RICHARDS: In connection with Mr. Reed's statement that the energy absorbed in electrolytic dissociation is measured by the heat of dilution, and that it is not to be connected with the energy of decomposition, I remembered having made some observations to the same effect before the Franklin Institute in March, 1896, in connection with a mechanical conception of what the dissociation theory might mean, which I will briefly repeat.

The term dissociation is unfortunate as regards the explanation of electrolysis, because to the chemist it is associated with the

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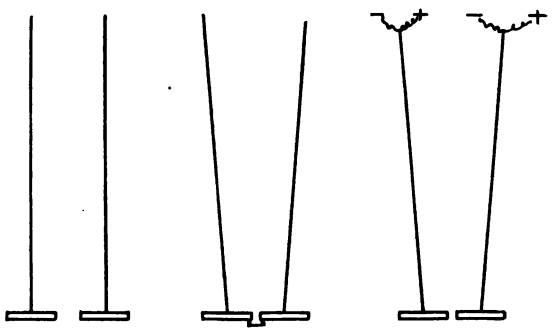
idea of chemical disruption, where the ingredients of the compound are actually chemically separated; and particularly to the student, the dissociation theory is understood or misunderstood as meaning that the ingredients of the compound are actually dissociated in the chemical sense. It is true that when the ingredients of a compound come together there is a large amount of heat set free in their combination. When we dissolve the compound in water and it is electrolytically dissociated, there is no evidence whatever that any energy has been supplied to dissociate the compound in the chemical sense. I believe that after electrolytic dissociation, so-called, has taken place, the compound is as firm a *compound* as it was before. The mechanical illustration



which I employed was this (see accompanying figure). If we take two electromagnets and suspend them by conducting wires at some little distance apart, when no electric current passes through, they simply hang vertically. If you pass electric currents through them in similar directions they attract each other, and come together in the third position, with the strings converging as is shown, the magnetic force holding the two together. The same object can be accomplished without the magnetic force by having little hooks on them and putting a band across so that we may hold them together by the physical force of the stretched string as in case two. To my mind, the chemical compound, held together by a considerable force of energy, may be likened to the magnets held together by the physical bond of the string. Now, if at a given instant you can throw off this physical bond, and at the same instant send on the electric current, the two magnets are held together just as firmly as before,

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but by a different sort of force. A chemical compound has its ingredients held together by, let us call it, chemic forces, and to my mind the electrolytic dissociation of that compound means a *replacement* of that force by electric force. The force which holds the molecules together has been changed from one kind to another; it has not been altered in quantity. After the electrolytic dissociation the ingredients, held together by electric force, are then controllable by electric energy, and may be finally disrupted by electric current. So that, as regards electrolytic dissociation, I have made the picture of it in my mind as being a change in the form of the energy which holds the compound together but not in its *amount.*

MR. HERING: I would like to ask Professor Richards whether he has extended his analogy to also explain that at the moment when the ions become molecules the heat of combination has to be supplied. I refer to what in some books is called the ionization heat.

MR. POTTER: There is a real physical difference between a solution in which ions are present and one in which they are not.

In the case of a colored solution the color may change if the dissociation becomes complete. Therefore, it would seem that any theory which involves the same geometrical relation of the component parts of the dissociated molecule, is faulty, and that there is a change in the distance between the component parts of the molecule effected by solution, but not a change of the energy relationship, nor necessarily a change in the chemical relationship, but a change like an opening-up of the entire structure.

PRESIDENT RICHARDS: *Ionization* is synonymous with *electrolytic dissociation*, as I understand it, and the term *ionization heat* does not refer to the chemical heat of combination, but to what has been called the *heat of electrolytic dissociation.* The separation of molecules into charged ions is, according to my manner of looking at it, merely a change of the *form* of energy uniting the components of the molecules, and not of its *quantity.* Ostwald has measured for a few substances what he calls the "*dissociation heat,*" that is, the amount of energy absorbed or evolved when molecules dissociate into charged ions, but the values obtained are small, and uncertain because of the number of unproved as-

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sumptions made in his calculations, and his neglect of the heats of dilution of the substances used.

After the molecules are "ionized," that is, the energy of their formation resolved or transformed into the energy of electrical charges on their constituent ions, then the compound is susceptible of being disrupted by the application of electrical energy, of potential sufficient to neutralize the electrical charges of the ions and in quantity equal to the energy of formation of the molecule. This is the place where the energy of formation may be supplied to extract from the compound the constituent elements from which it was originally formed. This electrical energy disappears at the electrodes, and it is there that the energy formerly evolved in the union of the constituents to form the molecule is restored to the system and the constituents restored to their original condition before combination.

MR. COWLES: When one forms a solution, the density of the materials employed becomes altered. Hence we may consider that there has been a change in the distance between the various molecules, and probably between the atoms in the molecules. Therefore, there has been a change in the gravitational potential energy within the mass as a system. Now, this calls for a giving up of energy in cases of condensation, which energy may not all escape from the mass of the liquid. Some of it may be spent in disrupting some of the molecules, and forming their constituents into ions. It remains potentially stored, or it is kinetic through their increased motion. The tendency of the parted ions to reunite, creates a back pressure, which is balanced by the gravitational pressure that would otherwise cause further condensation. The parted ions would be classed as dissociated under the theory of electrolytic dissociation. Everything is still in balance. Now throw sufficient electric stress on the mass to cause added molecules to dissociate. Energy must be supplied to the extent of such added dissociation, and the effect of adding to the swarm of free ions, is to throw them into greater activity, which enables the positive ions, with their electric charges, to float or be attracted to the negative surface, the cathode, where they give up their charges, and the negative ions to drift or be attracted towards the positive surface of the anode, where they give up

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their negative charges. I would ask if this is in harmony with the conception of Dr. Richards. It seems to me it is.

PRESIDENT RICHARDS: It is; my picture of the different ions in the solution is not that they are floating separate from each other, but that there is still an energy bond between them which is as firm, measured in energy units, as it was before they were ionized.

MR. COWLES: They may not float separate from each other; they are merely dodging in between each other in their floating.

MR. POTTER: I would like to draw an analogy in line with this in regard to the phenomenon known as water of crystallization in which a substance exists in a certain physical state, and you add water and it crystallizes. The water enters and produces a structure that is different. We can conceive that a molecular structure can exist in which the water enters the structure in solution, just the same as the water of crystallization enters a solid body.

MR. JOHNSON: This analogy of Mr. Potter would explain very well the influence of the solvent on the dissolved substance. It would give a mechanical analogy of the influence of the solvent on the dissociation, and how the electromotive forces in different solutions are affected by the nature of the solvent; this, together with the thought of the president, clarifies the situation greatly, in harmonizing certain facts which we know are in accordance with this dissociation theory and certain facts which we know are in accordance with chemistry in general.

PROF. W. D. BANCROFT (communicated): While the experimental facts are interesting, I fail to see that they prove anything. Even if we admit the accuracy of the author's calculations, the results are vitiated by the use of porous diaphragms. I think it probable that the effect due to electrical endosmose exceeds the effect due to the electrolytic transference and the author has ignored this factor completely.

MR. C. J. REED (communicated): I regret that illness prevented me from remaining during the reading and discussion of this paper. The discussion shows some misapprehension of the purpose of, and the facts described in, the paper.

The total electromotive force between the terminals of the

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apparatus did not exceed 8 volts and the expenditure of energy was, therefore, less than 5 watts. The solution in compartment 4 was identical in composition, form, and dimensions with that in compartments 2 and 3, and its resistance could not, therefore, have been materially different at the beginning of the experiment. During the progress of the experiment the resistance of compartment 4 diminished as the solution increased in density and approached the maximum conductivity of sulphuric acid. Consequently, for a given current less heat was generated in this compartment than in any other compartment and in the others there was no increase of volume or other indication of increase in temperature. Any one who considers that the total energy expended in the entire apparatus (a thin glass tube $1^1/_4$ inches in diameter immersed in water maintained at 9° C.) was only 5 watts, cannot conclude that there was any appreciable elevation of temperature in any part of the tube.

But the question of the effect of change of temperature in this experiment is entirely eliminated by the fact that all the measurements made were independent of the temperature, the volumes having been measured and the solutions weighed outside of the apparatus and at the temperature of the room. It is idle to speak of the temperature having caused this increased weight and volume of the solution in compartment 4.

In answer to Mr. Cowles I would refer to the last two paragraphs of the paper, which were omitted by a clerical error, from the paper read at the meeting, and which show that the effect of osmosis alone in this experiment was inappreciable.

Referring to the communicated statement of Dr. Bancroft, it appears to me rather ungenerous to question the accuracy of experimental data carefully and laboriously made, or to say that they prove nothing, without attempting to verify or disprove the figures. He states that the results are vitiated by the use of porous diaphragms, yet he does not say in what manner they are vitiated. He ascribes the result entirely to the effects of "electrical endosmose," but he does not say what electrical endosmose is, nor does he give us means by which its effects may be predicted or determined. So far as I am able to learn, electrical endosmose is only a term invented to express our ignorance of the very phenomenon I have described, and to enable us to ignore

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or avoid it in considering the theory of electrolytic dissociation. The fact remains that the phenomenon described is not accounted for and could not be predicted by the theory of electrolytic dissociation. I may call attention also to an additional fact in this connection. It is that the porous diaphragms produce no vitiating effect when only a single electrolyte is used, as is shown in compartments 1, 2 and 3 in my experiment. In addition to this evidence, I performed another experiment with the same apparatus, using the same sulphuric acid solution in all compartments and using platinum electrodes. In that case the migration of SO_4 throughout the entire apparatus was exactly according to the migration constant used in my calculations for the requirements of the theory of electrolytic dissociation, which were obtained by interpolation from Hittorf's data, showing that with the same electrolyte on both sides of the diaphragm there is no "vitiating" effect, and showing clearly that the unexpected phenomenon is due to the passage of the current across the junction of the two different electrolytes and to nothing else; since neither the diaphragm with two electrolytes and no current, nor the diaphragm and current with one electrolyte can produce any "vitiating" effect.

In this experiment with the H_2SO_4 solution in all compartments the following data were obtained:

Duration of experiment	7	hours
Current measured by ammeter	0.80	ampere
Increase in weight of cathode of copper voltameter in circuit	6.676	grams
Total ampere-hours $\frac{6.676}{1.18} =$	5.65	
Loss of SO_4 in compartment 1 (cathode)	4.15	grams
Increase of SO_4 in compartment 2	0.23	"
Increase of SO_4 in compartment 3	0.01	"
Increase of SO_4 in compartment 4	0.20	"
Increase of SO_4 in compartment 5	0.10	"
Increase of SO_4 in compartment 6	4.20	"

The mean change in concentration at the electrodes is the mean of 4.15 and 4.20 or 4.175 grams of SO_4, and the migration constant is $\frac{4.175 \times 2}{2 \times 5.56 \times 0.03729 \times 96} = 0.208$, while that assumed in my calculations for the requirements of the theory was 0.2.

It was not my purpose in presenting these facts to state that they

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prove or disprove the theory of electrolytic dissociation or any other theory, but to give the proponents of that theory an opportunity of rationally reconciling these facts with the theory. It seems to me incumbent upon the advocates of any theory to give a better explanation for facts than merely to dismiss them with a name invented for the purpose of avoiding the issue.

The remainder of the discussion following the paper does not appear to require any reply from me.

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A paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 18, 1902, President Richards in the Chair.

ELECTROCHEMICAL POLARIZATION.

By JOHN W. LANGLEY.

An interesting paper with the above title was communicated by Mr. C. J. Reed to the Franklin Institute, and printed in their Journal, April, 1902. His conclusion is that this phenomenon is due wholly to chemical changes produced in the system by the current, and he gives the following definition: "Polarization is most correctly defined as a progressive change in the composition and electromotive force of an electrochemical system necessitated by the progressive exhaustion of one or more of the electrochemical reagents." With the general sense of the above definition I am disposed to agree, but I take exception to the importance given to the idea of progression as an essential part of the phenomenon. Mr. Reed discusses the case of a copper and a zinc plate immersed each in a solution of its own sulphate, and having the solutions separated by a diaphragm. This is essentially a Daniell's or gravity-cell. In this case the continual passage of a current sent in from an external source will finally result in changing all of the liquid into either copper sulphate, or into zinc sulphate, depending on whether the copper or zinc is made the anode plate of the electrolytic cell, with, of course, a change in the polarization value of the electromotive force from the 1.09 volts of the initial state to that of nearly zero potential when both plates by metallic deposition present either two copper surfaces in a solution of cupric sulphate, or two zinc surfaces in a solution of zinc sulphate. This is the final or stable condition of the cell, and it will be permanent so long as the anode plate is not wholly dissolved. In this case it is true that the polarization value of the cell progressively changes, with a tendency to become nearly zero after a very considerable lapse of time, but the phenomenon of polarization is generally considered to occur instantaneously upon the passage of a current through an electrolyte, and it usually reaches a limiting value very soon. The solution

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begins to be altered at the face of each electrode instantaneously, this change being always of such a character as to make the cell act as a primary battery with its electromotive force opposed to that of the electromotive force which is driving the electrolyzing current. This is true even in the case of the so-called non-polarizable electrodes which consist of two plates of the same metal immersed in a salt of that metal, *e. g.*, copper in a solution of copper sulphate or zinc in a solution of zinc sulphate, for it is well known that phenomena of concentration and dilution occur at the faces of the electrodes. Some years ago the writer covered the faces of two copper plates with a thin film of cellulose dissolved in cuprammonium and then precipitated the cellulose by hydrochloric acid. This deposited on the plates a porous insoluble covering about a fifth of a millimeter thick. On immersing these plates in a solution of copper sulphate and passing a current the well-known increase of density at the anode and diminution at the cathode took place, and on withdrawing the plates the porous cellulose films brought away samples of the liquid adjacent to the face of the electrode which could be separately analyzed. In this way it was found that for the thickness of the films used and the density of the current employed the solution at the anode contained approximately six times as much copper as that at the cathode. Somewhat similar results were found for zinc, and also for these metals when their chlorides and nitrates were substituted for their sulphates.

This difference of concentration makes of the cell a primary battery belonging to the type which has one metal and two liquids. Its electromotive force is exceedingly low, but it is opposed to that of the electrolyzing current.

Since the result of the polarization is to make the electrolytic cell act as a battery, the counter-electromotive force may be measured by some of the standard methods used for actual primary batteries. A study of this phenomenon was made by two of my students and embodied in a thesis having the title "The Counter-Electromotive Force of Electrolytic Deposition Cells at Potential Differences Ranging between the Maximum Polarization Voltage and Zero."

The method consisted in passing a current through an electrolytic cell and by means of a quick-acting commutator interrupting

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the feeding current and then almost instantaneously putting the electrodes in series with a condenser, and then breaking circuit between the electrodes and the condenser and discharging the latter through a ballistic galvanometer. The commutator was arranged to do all this by a single movement of the switch, and in a very brief interval of time. The observer thus obtained the voltage of the charging current, and about one-tenth of a second later the counter-electromotive force caused by the chemical products corresponding to the polarization.

I quote one table of observations as an illustration of the method. All of the substances experimented on were recorded in the same way.

The first column gives the voltage of the electrolyzing or feeding current which produced the chemical decomposition. The second column gives the discharging value of the polarization voltage, practically on open circuit, because of the use of a condenser. The electrodes were twelve square centimeters in area.

Platinum electrodes in a 10 per cent. solution of potassium sulphate in distilled water.

Applied volts of the electrolyzing current.	Electrode volts, electromotive force of discharge.
0.43	0.415
0.60	0.597
0.99	0.988
1.21	1.189
1.39	1.341
1.57	1.48
1.77	1.692
1.97	1.881
2.16	2.07
2.35	2.189
2.56	2.32
2.75	2.381
2.94	2.43
3.16	2.446
3.35	2.446

It will be noted that while the polarization voltage rises with an increase of the charging voltage nearly linearly to 2.00 volts, it then increases less rapidly, and finally reaches a constant value at 2.446 volts. The curve, Fig. 1, shows this relation. Fig. 2 gives the behavior of solutions of sulphuric acid in water, one-

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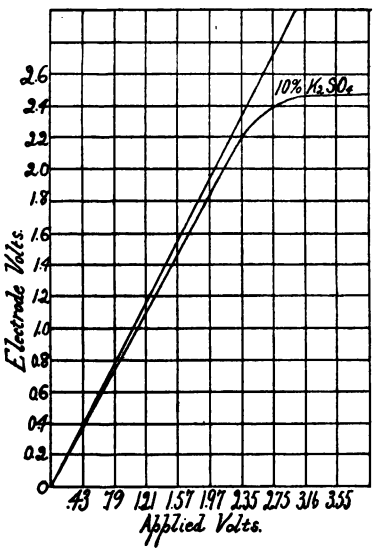

FIG. 1. Potassic sulphate.

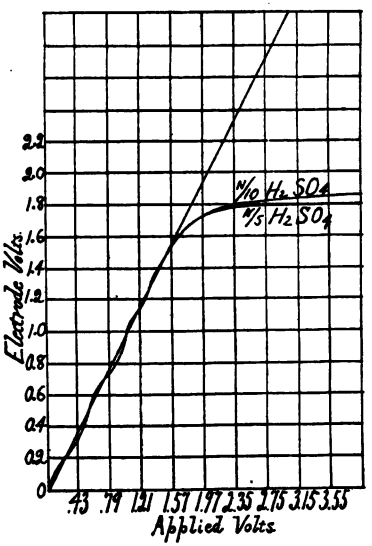

FIG. 2. Sulphuric acid.

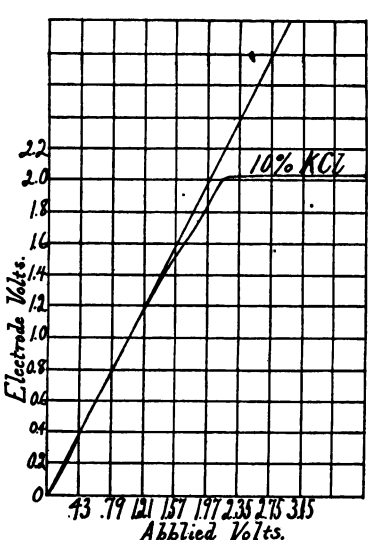

FIG. 3. Potassium chloride.

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tenth normal and one-fifth normal respectively; Fig. 3 denotes the counter-electromotive force of a neutral solution of potassium chloride in water. With the so-called non-polarizable electrodes, the general character of the phenomena is the same, only, of course, the counter-electromotive force is much lower.

When two copper electrodes were immersed in a 10 per cent. neutral solution of cupric sulphate the polarization increased with the applied volts and finally became constant at 0.037 volt for the counter-electromotive force. When this solution was slightly acidulated with sulphuric acid the maximum polarization rose to 0.067 volt.

With zinc electrodes in a 10 per cent. zinc sulphate solution the point of constant polarization was 0.061 for the neutral, and 0.085 for the acidulated liquid.

In the above cases the maximum current was about one-tenth of an ampere, which corresponded to a current density of $^1/_{120}$ of an ampere per square centimeter, or $83^1/_3$ per square meter.

In the electrolysis of fused salts the same phenomena are observed. Two other students investigated this, using a carbon-lined iron pot of about three gallons capacity, and a carbon rod three inches in diameter and fifteen inches long for an anode, the current was 1000 amperes and the liquid was alumina dissolved in fused cryolite. This was the method of heating. The measurements were made on two smaller carbon electrodes immersed in the melted mass and polarized by a current from a storage battery.

For fused sodium chloride and fused potassium chloride, an iron pot heated in a gas furnace was used; the pot was made the cathode, and a half-inch carbon rod the anode.

The result is shown in Figs. 4, 5, and 6. As it was impossible to wholly exclude oxygen from the melted mass, and as the salts were not chemically pure the polarization values are not given as being absolutely correct, but only as representing the approximate voltages which will be encountered in commercial working using carbon anodes, and at the temperatures here employed which were, for the alumina, 1010°; for sodium chloride, 900°; and for potassium chloride, 750° centigrade.

Mr. Reed's Franklin Institute paper, already referred to, quotes seven differing definitions of polarization from various authors,

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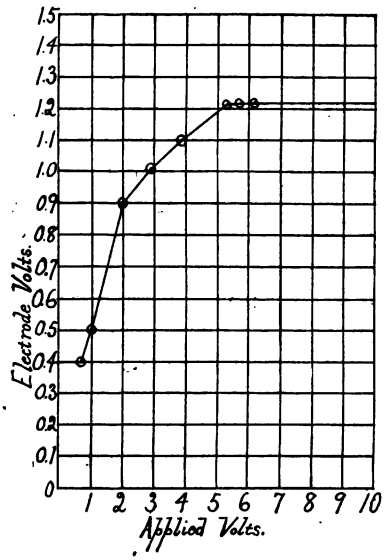

FIG. 4. Alumina in melted cryolite. Temperature, 1010° C.

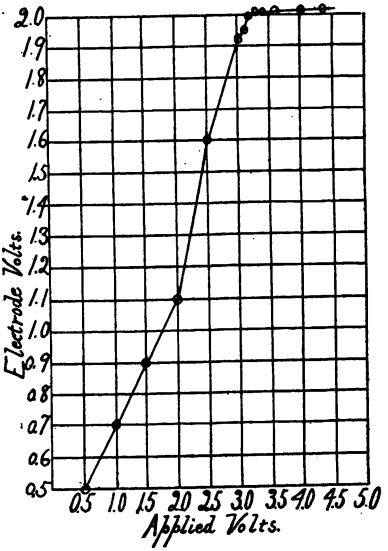

FIG. 5. Melted sodium chloride. Temperature, 900° C.

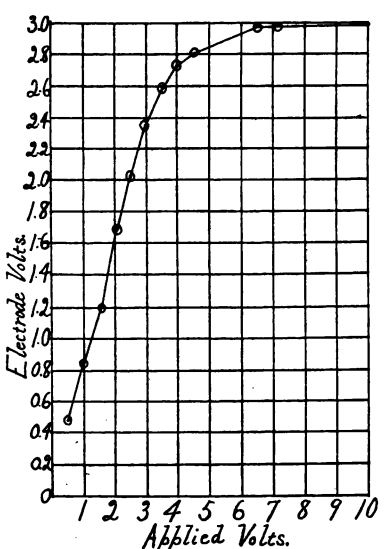

FIG. 6. Melted potassium chloride. Temperature, 825° C.

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some of whom consider a change in resistance to be part of the phenomenon; thus Newman defines it as "Increased resistance of the cell and consequent falling off of the current." Newberger says "By polarization is meant any phenomenon, or the sum of all phenomena, which require an increase of voltage during electrolysis. These phenomena are (*a*) deposition of gases at the electrodes, whereby the gases cause an opposite current through the electrolyte; (*b*) the resistance of very dense layers of gas between poles and electrolyte; (*c*) changes of concentration in the electrolyte; (*d*) changes of temperature."

The view taken by the writer of this paper is opposed to considering ohmic resistance as forming any part of electrochemical polarization. It can no more cause a counter-electromotive force capable of giving a discharge than can the "drop on the line" in a copper wire restore to the circuit the voltage thus lost, and the *change* in resistance caused by chemical polarization is analogous to the temperature coefficient of resistance in a solid conductor. If, then, ohmic resistance is to be excluded, and also the heating effects due to this resistance, it remains to specify what changes are included properly in the term "electrochemical polarization," and how its value is to be determined.

The method by discharge seems to be the only one, but here the question arises: Is the polarization to be measured by the instantaneous value of the stored energy, or rather should it be regarded as the instantaneous value of the counter-electromotive force existing *during the passage of the electrolyzing current?*

It is the writer's belief that the latter condition is the correct one, and if this is so, then it is demonstrable that the method by discharge will always give too low results, although these may be made to approach exceedingly near to the true value of the opposing force. By the condenser method the product of the current by the time during which the discharge from the cell is taking place, that is, the quantity Ct is so very small that the effects of ohmic resistance become negligible, but the chemical products of the change, if they are gaseous or liquid, are diffusing away from the faces of the electrodes. The phenomena of concentration already quoted prove this; therefore, any interval, however short, between cutting off the electrolyzing current and cutting in the condenser will cause a loss, very small, it is true,

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but it will be always greater than zero. The constant point of maximum discharge polarization shown by the curves apparently occurs when the entire stratum on the face of the electrodes, and of a thickness of at least the radius of molecular attraction is occupied solely by the chemical substance at that face; *e. g.*, for pure water, a *solution* of oxygen at the anode and a solution of hydrogen at the cathode. Prior to this time the film is only partly composed of the substances, some of the original liquid still being present.

Another exceedingly small cause of a greater electromotive force on charging than on discharging is caused by the velocity of the ions being accelerated above their average during the last few millionths of an inch from the electrodes. This will cause a slight thermal rise due to impact, thus taking energy from the circuit which cannot be restored on discharge, but both of these conditions taken together, the diffusion and the thermal, will probably not exceed two or three millivolts when a quick-acting commutator is used. Returning now to Mr. Reed's definition quoted in the first part of this paper, it is evident that electrochemical polarization is progressive in amount as long as the electrolyzing current is gradually raised to the point where the counter-electromotive force becomes constant, then it is no longer progressive, also, that if a large current is employed at the beginning, then the point of constant polarization will be attained in a very brief interval of time. In both cases the polarization will remain at its maximum value and constant indefinitely so long as the general mass of the electrolyte does not change its composition.

In conclusion, the writer holds that electrochemical polarization is caused by chemical changes and is not related to ohmic resistance; that it reaches its maximum whenever these altered products occupy the whole face of the electrodes and to a depth of at least one radius of molecular attraction; and finally, that its maximum value is attained only when the electrolyzing current which produces the decomposition is actually passing, but that for practical purposes we may measure this quantity by taking its discharge electromotive force on open circuit.

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DISCUSSION.

MR. A. H. COWLES: Mr. President, I have listened to this paper, and I have read Mr. Reed's paper when it was published some time ago. It seems to me that Dr. Langley and Mr. Reed are both looking at the same problem, and arriving at the same conclusion, only their points of view are from two sides of what I might call a molecular division. Dr. Langley attributes the voltage absorbed to the algebraic sum of the electromotive forces created by the chemical products freed, while Mr. Reed brings an electric stress upon the electrolyte, just up to the tension where molecules begin to disrupt, and added ions become freed. These, collecting at the electrodes, create electromotive forces whose algebraic sum just balances the voltage pressure of disruption.

Perhaps I can make a mental picture of that which would illustrate my view of what constitutes voltage of disruption, by drawing an analogy to the phenomena of disassociation. Imagine a mass of some compound heated exactly to the temperature of disassociation. Imagine that one molecule dissociates. It consumes energy and relieves the heat stress slightly on the whole mass. The heat strain drops a notch, more heat is thrown into the mass and it raises a minute notch. That added notch causes the breaking of another molecule and its atoms are thrown asunder. So it is that the stress on the whole mass causes a single molecule to break, and then another, and another, by minute jerks. In this you have an analogous action to that which occurs when the electric stress disrupts the succession of molecules with the formation of ions when the electric pressure is gradually elevated and thrown on to a conducting liquid. The electric tension on the whole mass of molecules whose individuals are floating in a dielectric, increases until you reach the point where the first molecule disrupts, and its atoms increase the swarm of ions on the electrodes. This occurs when the increasing electric pressure just reaches the voltage of disruption. Ions now begin to collect at the anode and cathode and create a counter-pressure against the flow of the current, by their tendency to recombine, which is felt through the whole mass. This counter-electromotive force is in balance with and is a true measure of the voltage of disruption, but in order that the current shall be able to overcome it, and the freeing of ions continue, electric pressure must be added in ex-

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cess of this counter-pressure, and the excess of pressure thus thrown on the cell causes measurable current to flow, and an absorption of energy which manifests itself as heat evolved in the liquid, as though from ordinary ohmic resistance.

Gas films that may form between the electrodes and liquid, also introduce ohmic resistances, which interfere with measurements of true counter-electromotive force. Again, there may be local galvanic action at the electrodes that alters the potential of their different parts. Take for example, the electrolysis of alumina that was described as being performed in a carbon crucible, where molten cryolite is employed containing alumina, and a carbon anode is introduced above molten aluminum resting on the carbon bottom. Here we have liquid aluminum in the bottom of the carbon cup, and in contact with carbon. When you have a non-corrodable conductor in contact with a metal, and a liquid that will corrode the latter, you have a galvanic couple. I have found by experiment, that cryolite corrodes or dissolves aluminum. Wherever there is carbon in contact with this molten aluminum, Dr. Langley had a local galvanic couple, with the result of current flowing from the aluminum through the electrolyte to the carbon walls, thus producing a sort of vortex of electric current, through the center of which the main electrolyzing current had to flow. The effect of these local currents is to alter the potential of the cathode, so that measurements of differences of potential between the anode and cathode cease to be exact, as recording the true voltage of disruption of alumina, which was the final product that was broken down in this experiment of Dr. Langley's. In this instance 2.83 volts should be absorbed in disrupting alumina, 0.62 of a volt is generated in the formation of CO at the anode, the difference 2.21 volts should be the counter-electromotive force of this cell, while Dr. Langley found as low as one volt's fall of potential between anode and cathode, causing current to flow. As I view it, this lower possible measurement is because of this local action, which prevents the production of the full theoretical amount of aluminum according to Faraday's law.

I cannot agree with Dr. Langley, that alumina itself is an electrolyte. However, of all the compounds present in the bath in his experiment, it has the lowest heat of combination, and, there-

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fore, whatever may be the electrolyte, as a final result of the affinities involved, aluminum and oxygen part company.

MR. CARL HERING: Mr. Reed, who had to go home because he was taken ill, has asked me to say in his behalf that Prof. Langley misunderstood the statements which Mr. Reed made in his former paper. He did not have time to go into further explanation.

MR. COWLES: That is my view exactly, that they are in agreement, but they do not realize that they are in agreement.

MR. H. N. POTTER: I do not wish to criticize the results of the paper, but I would like to say in regard to the method, that we have here admittedly a short time interval which elapses between the breaking of the current, and the charging of the condenser. This interval due to the construction of the switch, is indefinite. Therefore after all the results are accomplished, one must introduce a slight element of doubt as to what the effect of this short interval of time is.

If, instead of using the Ballistic galvanometer, we should use a zero method for measuring, and balance the force of polarization by a known electromotive force, and should then substitute for the switch a rotating commutator, the speed of which can be changed, we can then start by measuring the voltage one second after the charging current is interrupted, also, let us say, a thousandth of a second afterwards, with intermediate intervals, and get a progressive curve showing the effect of this time element. If the curve toward the end is virtually constant, we can fairly assume that the remaining thousandth of a second is producing practically no effect.

MR. COWLES: The heat of disruption of alumina is about 2.83 volts. Now, if it is a strain on the molecule up to the voltage of disruption, why does not that represent 2.83 volts before you get any current flowing? Of course, there is that cyclone of currents helping the main current along and you will measure a voltage lower than the voltage of disruption between the two poles. Otherwise I cannot understand how it is that they get such low voltages when you pass a current through the solution of alumina. But I can understand it on theoretical grounds if there is a liquid galvanic action between the accumulations in the bottom of the

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crucible and the carbon side walls. The aluminum on the bottom dissolves. It does not produce the full efficiency and the current goes through the liquid, through the carbon back to the aluminum, thus forming the cycle in that way, while the central current is going down to the bottom and depositing.

MR. POTTER: I should have said that the pot and anode were merely the heating devices and that the measurement was made with separate carbon electrodes. The electrode volts were nine-tenths at the first bend in the curve, the curve then ran at a different angle until the applied voltage was 5.1 when the electromotive force of polarization measured 1.121.

PRESIDENT RICHARDS: The term polarization, as used by Professor Langley, seems to me identical with counter-electromotive force. I have had a different idea of the meaning, or scope of the term, and have thought of the term polarization as different from counter-electromotive force, and being principally the increase of the resistance, which is due to the formation of a non-conductor at the electrodes, usually a gas, which covering part of the electrode, increases the resistance of the current in passing into the electrolyte, and thus increases the resistance of the cell. That, I think, is what has been frequently alluded to as polarization, especially in cells. If we use the term polarization as equivalent to counter-electromotive force, then I agree entirely with the description of it and explanation as given by Dr. Langley.

MR. POTTER: It seems to me that there are always two schools of thought, one that tries to give a definition against which no objection can be brought, and the other which tries to give us a mental picture of what really goes on. I think we ought to be thankful for those who produce the pictures, which have a great pedagogic value, even if they can not be demonstrated to be more than pictures.

If we can once state a thing so that there will be no objection to it, though it forms no mental picture, that is also distinctly an advance.

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A paper read by title at the Second Meeting of the American Electrochemical Society, Niagara Falls, September 18, 1902, President Richards in the Chair.

A CONTRIBUTION TO THE ELECTROCHEMISTRY OF BARIUM COMPOUNDS.

By Max M. Haff.

The recent successful extension of electrochemical methods to the industrial manufacture of the barium compounds, such as the electric furnace method used by the United Barium Company, has led to renewed interest in the details of such manufacture. For a description of the above-mentioned process, I would refer to the paper of Mr. Chas B. Jacobs, in the Transactions of the American Institute of Electrical Engineers, for Feb. 28, 1902. Since the separation of the crystalline barium hydrate in this process, by cooling the solution, is of capital importance to the method of manufacture, I have thought that some carefully determined data as to the freezing-points of such solutions and their specific gravity for differing percentages of hydrate,—as obtained in the course of our laboratory work and practice at Niagara Falls,—will be of interest to electrochemists who are following the developments of this process.

Strength of BaH_2O_2 Solutions at 80° C. by Volume and Weight.

Sp. gr.	Per cent. BaH_2O_2. (Vol.)	Per cent. BaH_2O_2. (Weight.)	Sp. gr.	Per cent. BaH_2O_2 (Vol.)	Per cent. BaH_2O_2. (Weight.)
1.514	58.22	38.45	1.219	24.53	20.12
1.500	56.31	37.54	1.200	23.00	19.17
1.479	54.14	36.60	1.195	22.15	18.53
1.458	49.38	33.87	1.174	19.83	16.89
1.450	48.90	33.72	1.152	17.78	15.43
1.413	45.99	32.55	1.129	16.01	14.18
1.400	45.00	32.14	1.125	15.80	14.04
1.390	44.22	31.81	1.114	14.56	13.07
1.375	42.40	30.84	1.100	13.06	11.87
1.368	41.45	30.30	1.076	10.58	9.83
1.350	38.60	28.59	1.062	9.16	8.62
1.338	37.30	27.88	1.049	7.55	7.20
1.312	35.02	26.69	1.040	6.51	6.26
1.301	34.02	26.13	1.031	5.18	5.02
1.278	31.48	24.67	1.022	4.78	4.67
1.249	28.14	22.52	1.015	3.90	3.84
1.236	26.41	21.36	1.009	3.37	3.34

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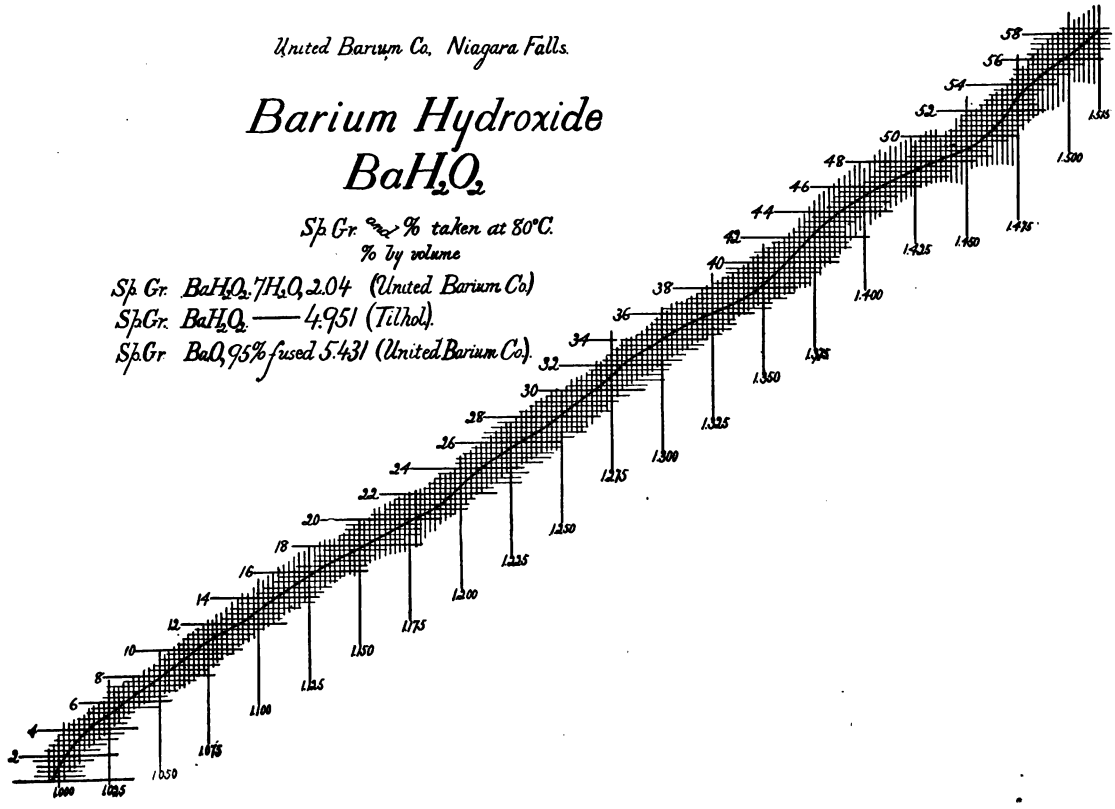
United Barium Co. Niagara Falls.

Barium Hydroxide
BaH_2O_2

Sp Gr $\frac{BaH_2O_2}{H_2O}$ % taken at 80°C.
% by volume

Sp. Gr. $BaH_2O_2.7H_2O$, 2.04 (United Barium Co)
Sp Gr. BaH_2O_2 —— 4.951 (Tilhol).
Sp Gr BaO, 95% fused 5.431 (United Barium Co).



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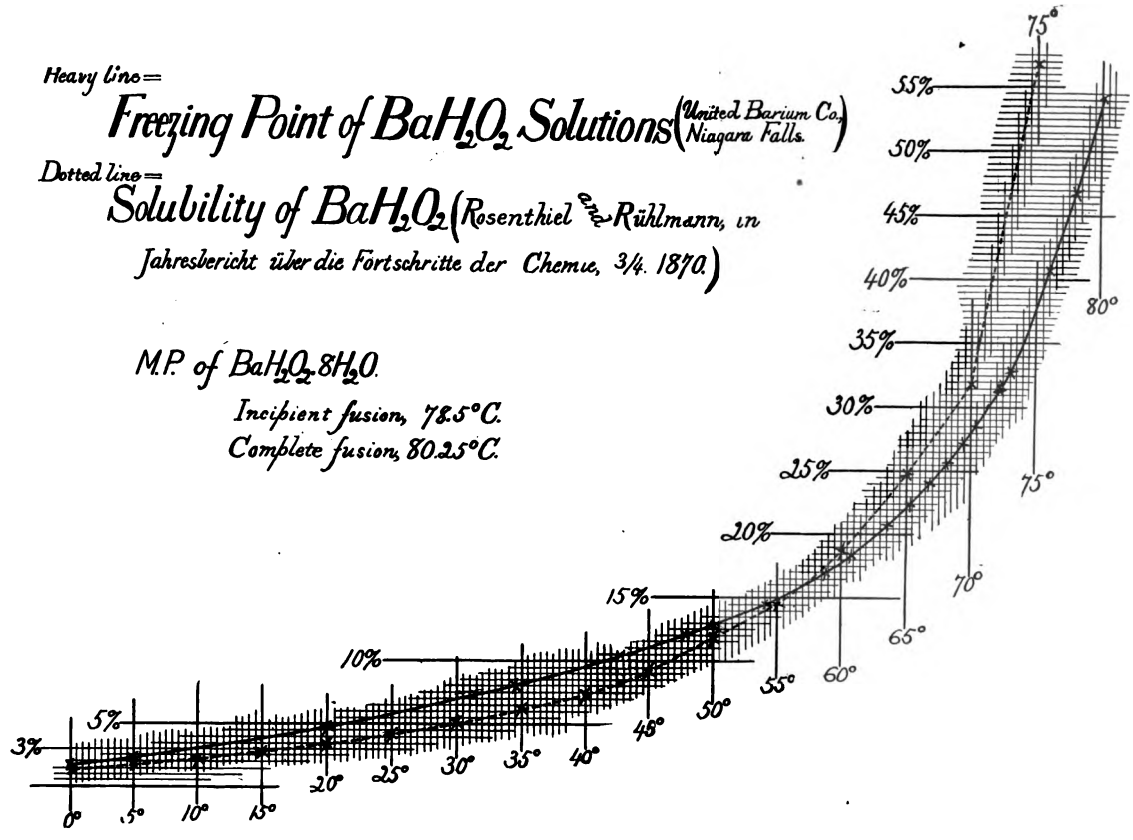

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FREEZING-POINT OF BaH_2O_2 SOLUTIONS.

Per cent. BaH_2O_2.	Degrees C.	Per cent. BaH_2O_2.	Degrees C.
54.23	80.0	18.4	60.6
46.7	78.0	16.9	58.8
40.7	76.0	14.8	55.0
32.7	73.0	12.0	47.6
31.3	72.2	10.4	42.7
28.6	70.3	8.2	34.5
27.1	69.2	7.0	30.0
25.6	68.1	4.8	20.0
24.0	66.7	3.0	9.5
22.4	65.3	2.25	5.0[1]
20.6	63.4	1.75	0.0[2]

[1] Saturated solution at 5° C. contains 2.1 per cent.
[2] Saturated solution at 0° C. contains 1.6 per cent.

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INDEX.

SUBJECTS AND AUTHORS.

Page.

Advances, Some, in the Closed and Continuous-Working Electric Furnace; Taylor 185
Anodes, The Electrolytic Dissolution of Soluble Metallic; Johnson 171
Bancroft, W. D., Discussions 61, 109, 129, 132, 147, 174, 193, 195, 215, 217, 250
Barium Compounds, A Contribution to the Electrochemistry of; Haff.. 267
Barnes, H. T., Paper, 197; Discussions.....204, 205
Battery Invention, Storage; Rodman 177
Blackmore, H. S., Discussion 84
Browne, D. H., and Vorce, L. R., Paper..... 219
Burgess, C. F., Discussion 147
Byrnes, E. A., Paper, 113; Discussions.....119, 120, 121
Cadmium, Differences of Potential between, and Various Solutions; Kahlenberg 89
Calculations, A Unit of Electrical Quantity for use in Electrochemical; Cowles 207
Calorimetry, Theory and Practice of Continuous-Flow Electric; Barnes 197
Carbon Electrodes, On the Testing of; FitzGerald..... 43
Carhart, H. S., Paper, 123; Discussions.....134, 145, 156, 194, 205
Carveth, H. R., Discussion..... 131
Catalogue of Members, Alphabetical, 9; Geographical..... 30
Cathodic Reduction; Weightman 65
Cathodes, The Phenomenon of the Formation of Metallic Dust from; Haber..... 189
Cells, Concentration, A Thermo-electric Theory of; Carhart 123
Cells, Voltaic, with Fused Electrolytes; Byrnes..... 113
Closed and Continuous-Working Electric Furnace, Some Advances in the; Taylor 185
Coho, H. B., Discussion 157
Concentration Cells, A Thermo-electric Theory of; Carhart..... 123
Conduction, Some Phenomena of Electrolytic; Reed..... 235
Continuous-Flow Electric Calorimetry, Theory and Practice of; Barnes 197

Digitized by Google

Continuous-Working Electric Furnace, Some Advances in the Closed and; Taylor 185
Cowles, A. E., Paper, 207; Discussions 170, 204, 215, 217, 218, 245, 249, 250, 263, 265
Developments in Electrometallurgy of Iron and Steel; Ruthenburg 93
Differences of Potential between Metallic Cadmium and Various Solutions; Kahlenberg 89
Dissolution, Electrolytic, of Soluble Metallic Anodes; Johnson 171
Dodge, N., Discussion 182
Doremus, C. A., Resolution by, 3; Discussion 110
Dust, Metallic, The Phenomenon of the Formation of, from Cathodes; Haber 189
Efficiency of Electric Furnace Operations; Richards 51
Electrical Quantity, A Unit of, for Use in Electrochemical Calculations; Cowles 207
Electric Calorimetry, Theory and Practice of Continuous-Flow; Barnes 197
Electric Furnace, Closed and Continuous-Working, Some Advances in the; Taylor 185
Electric Furnace, Fusion of Quartz in; Hutton 105
Electric Furnace Operations, Efficiency of; Richards 51
Electrochemical Calculations, A Unit of, Electrical Quantity for Use in; Cowles 207
Electrochemical Paradox, An; Hering 139
Electrochemical Polarization; Langley 255
Electrochemistry at the World's Fair, St. Louis; Goldsborough 153
Electrodes, On the Testing of Carbon; FitzGerald 43
Electrolytes, Fused, Voltaic Cells with; Byrnes 113
Electrolytic Conduction, Some Phenomena of; Reed 235
Electrolytic Dissolution of Soluble Metallic Anodes; Johnson 171
Electrolytic Plants, Pumps and other Accessories in; Browne and Vorce 219
Electrometallurgy of Iron and Steel, Developments in the; Ruthenburg 93
Electronic Hypothesis and its Applications, The; Reuterdahl 159
Fair, Electrochemistry at the World's, St. Louis; Goldsborough 153
FitzGerald, F. A. J., Paper, 43; Discussions 49, 110
Formation of Metallic Dust from Cathodes, The Phenomenon of; Haber 189
Furnace, Electric, Advances in the Closed and Continuous-Working; Taylor 185
Furnace, Electric, Efficiency of Operations in; Richards 51
Furnace, Electric, Fusion of Quartz in the; Hutton 105
Furnace, Operations, Efficiency of Electric; Richards 51
Fused Electrolytes, Voltaic Cells with; Byrnes 113
Fusion of Quartz in the Electric Furnace; Hutton 105
Geographical List of Members 30
Goldsborough, W. E., Paper 153
Haber, F., Paper, 189; Discussions 61, 83, 110, 129, 149, 193, 195, 196
Haff, M. M., Paper 267
Hart, E., Discussions 48, 61, 98, 100, 101

Digitized by Google

Hering, C., Paper, 139; Resolutions introduced by, 156; Discussions.. ..... 60, 82, 101, 130, 150, 151, 156, 215, 233, 245, 248, 265
Hutton, R. S., Paper, 105; Discussions.....48, 83, 86, 110, 146, 149, 204
Hypothesis, The Electronic, and its Applications; Reuterdahl..... 159
Invention, Storage Battery; Rodman 177
Iodide of Cadmium, Differences of Potential between Cadmium and; Kahlenberg..... 89
Iron and Steel, Developments in the Electrometallurgy of; Ruthenburg 93
Johnson, W. McA., Paper, 171; Discussions...99, 101, 145, 174, 233, 245, 250
Kahlenberg, L., Paper, 89; Discussions 130, 133, 148, 195, 203
Keith, N. S., Discussions..49, 82, 99, 101, 134, 174, 182, 183, 193, 196, 216, 232
Langley, J., Paper 255
Larchar, A., Discussion..... 183
List of Members, Alphabetical, 9; Geographical..... 30
List of Members Elected since April, 1902 6
Meeting, Proceedings of Niagara Falls..... 3
Meetings, Board of Directors, Abstract of Minutes of..... 6
Members, Alphabetical List of, 9; Geographical List of 30
Members Elected since April, 1902, List of 6
Metallic Anodes, The Electrolytic Dissolution of Soluble; Johnson 171
Metallic Dust from Cathodes, The Phenomenon of the Formation of; Haber..... 189
Obituary 29
On the Testing of Carbon Electrodes; FitzGerald..... 43
Operations, Efficiency of Electric Furnace; Richards 51
Paradox, An Electrochemical; Hering 139
Patterson, G. W., Discussion 131
Phenomena, Some, of Electrolytic Conduction; Reed..... 235
Phenomenon of the Formation of Metallic Dust from Cathodes, The; Haber..... 189
Plants, Pumps and other Accessories in Electrolytic; Browne and Vorce 219
Polarization, Electrochemical; Langley 255
Potential, Differences of, between Cadmium and Various Solutions; Kahlenberg..... 89
Potter, H. N., Discussions.....204, 245, 246, 248, 250, 265, 266
Proceedings of the Niagara Falls Meeting..... 3
Pumps and Other Accessories in Electrolytic Plants; Browne and Vorce 219
Quantity, A Unit of Electrical, for Use in Electrochemical Calculations; Cowles 207
Quartz, Fusion of, in the Electric Furnace; Hutton..... 105
Reduction, Cathodic; Weightman 65
Reed, C. J., Paper, 235; Discussions .....
78, 87, 100, 103, 119, 120, 132, 145, 182, 194, 195, 205, 216, 217, 235, 250
Resolutions passed 3, 156
Reuterdahl, A., Paper..... 159
Richards, J. W., Paper, 51; Discussions.....
..... 62, 87, 103, 133, 134, 149, 151, 196, 216, 234, 246, 248, 266

Digitized by Google

Rodman, H., Paper, 177; Discussions 83, 145, 183
Ruthenburg, M., Paper 93
Salom, P. G., Discussions 102, 103
Smith, E. W., Discussion 83
Soluble Metallic Anodes, The Electrolytic Dissolution of; Johnson 171
Some Advances in the Closed and Continuous-Working Electric Furnace; Taylor 185
Some Phenomena of Electrolytic Conduction; Reed 235
Sperry, E. A., Discussion 84
Steel, Developments in the Electrometallurgy of Iron and; Ruthenburg 93
St. Louis, Electrochemistry at the World's Fair at; Goldsborough 153
Storage Battery Invention; Rodman 177
Taggart, W. T., Discussion 196
Taylor, E. R., Paper 185
Testing of Carbon Electrodes, On the; FitzGerald 43
Theory and Practice of Continuous-Flow Electric Calorimetry; Barnes. 197
Theory, A Thermo-electric, of Concentration Cells; Carhart 123
Thermo-electric Theory of Concentration Cells, A; Carhart. 123
Treasurer, Informal Report of the 3
Unit of Electrical Quantity for Use in Electrochemical Calculations; Cowles 207
Voltaic Cells with Fused Electrolytes; Byrnes 113
Vorce, L. R., and Browne, D. H., Paper 219
Weightman, A. T., Paper, 65; Discussions 84, 86, 131, 132, 133
Whitney, W. R., Discussions 61, 109, 133, 169, 205
World's Fair, St. Louis, Electrochemistry at the; Goldsborough 153

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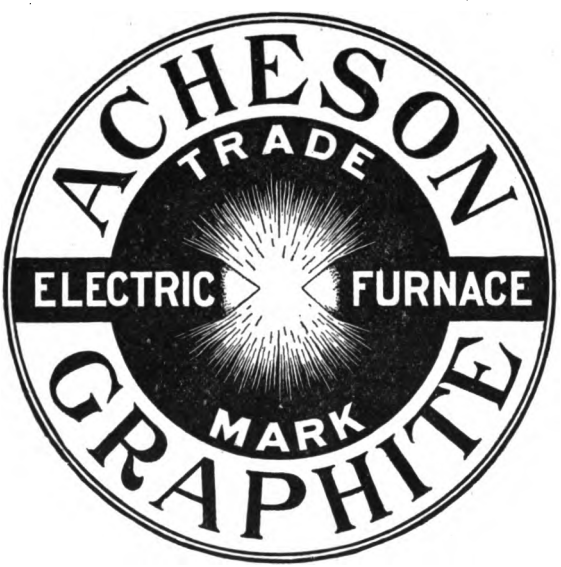

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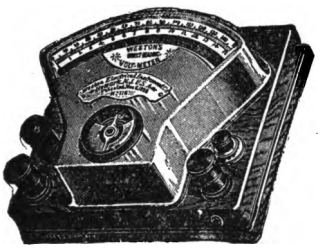

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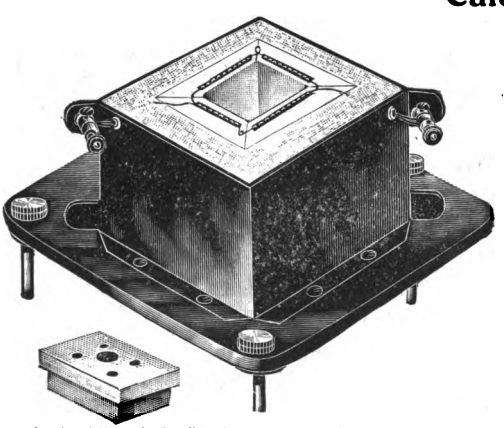

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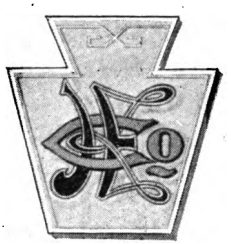

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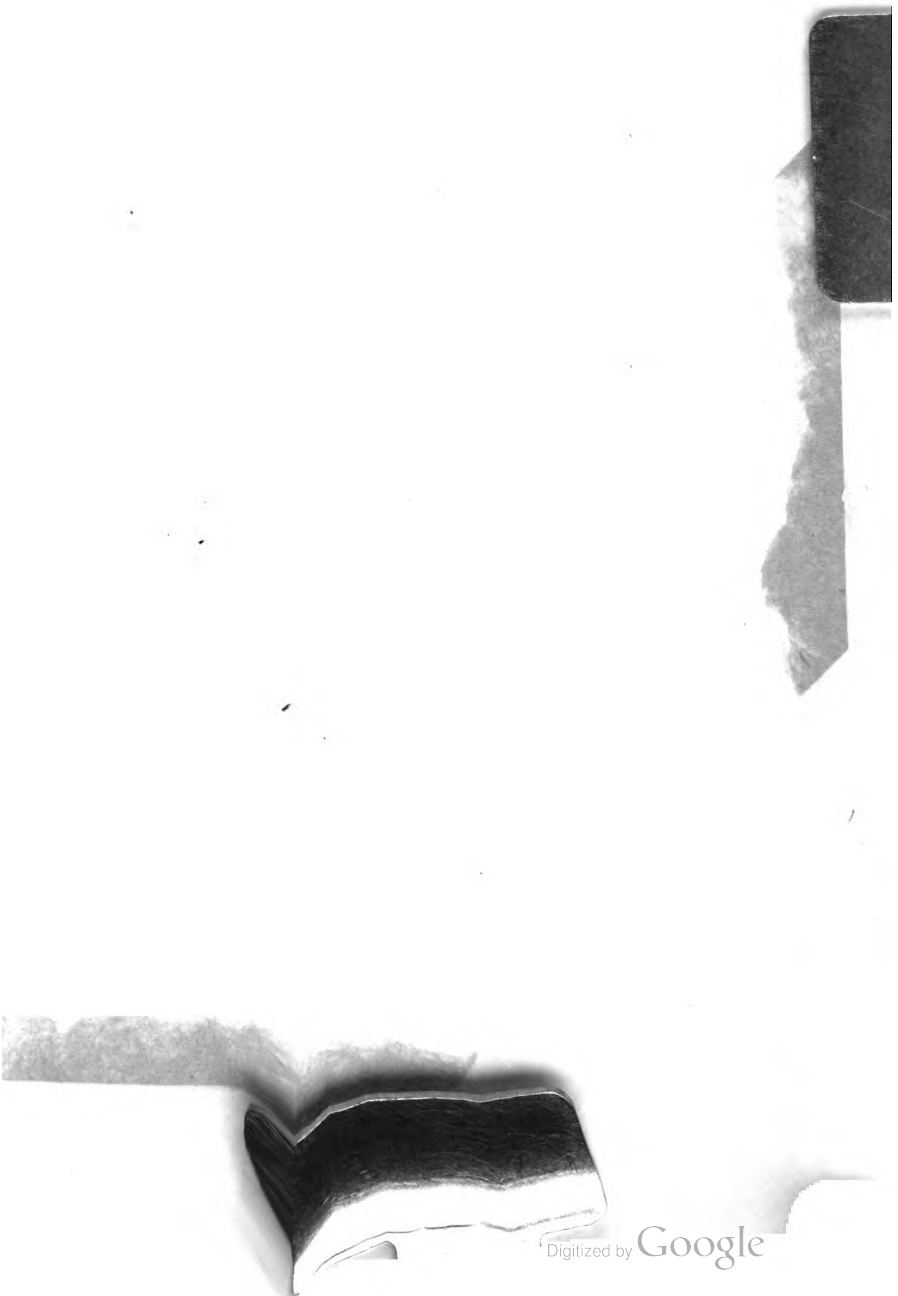

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